ISTANBUL TECHNICAL UNIVERSITY ★ GRADUATE SCHOOL OF SCIENCE ENGINEERING AND TECHNOLOGY

FABRICATION, CHARACTERIZATION AND ANTIBACTERIAL PERFORMANCES OF COMPOSITE POLYSULFONE MEMBRANES INCLUDING GRAPHENE OXIDE NANOPARTICLES

M.Sc. THESIS

Nurmiray YILMAZ

Graduate School of Science Engineering and Technology

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İSTANBUL TEKNİK ÜNİVERSİTESİ ★ FEN BİLİMLERİ ENSTİTÜSÜ

GRAFEN OKSİT NANOPARTİKÜL İÇEREN POLİSÜLFON KOMPOZİT MEMBRANLARIN ÜRETİMİ,KARAKTERİZASYONU VE ANTİBAKTERİYEL PERFORMANSI

YÜKSEK LİSANS TEZİ

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OCAK 2016

Nurmiray YILMAZ, a M.Sc. student of ITU Graduate School of Science Engineering and Technology student ID 513131017, successfully defended the thesis entitled "FABRICATION, CHARACTERIZATION AND ANTIBACTERIAL PERFORMANCES OF COMPOSITE POLYSULFONE MEMBRANES INCLUDING GRAPHENE OXIDE NANOPARTICLES", which she prepared after fulfilling the requirements specified in the associated legislations, before the jury whose signatures are below.

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Date of Submission : 27 November 2015
Date of Defense : 7 January 2016

To my family,

FOREWORD

In recent years, the membrane prosesses have been used in drinking water and also in wastewater treatment. The prosseses of membrane have lots of advantages but also have some disadvanteges. The new technologies have been applied for the disadvantages of membrane processes such as the production of resistant membranes and also using nanoparticles on membrane surfaces modification.

This study has been carried out in MEMTEK (Prof. Dr. Dinçer Topacık National Research Center on Membrane Technologies). I would like to express my sincere gratitude to many people for support during this project and study of thesis. Firstly, I would like to thank deeply my thesis advisor Prof. Dr. İsmail KOYUNCU for his guidance and suggestions during this study. I wish to thank Associate professor. Derya Yüksel KOSEOGLU IMER for invaluable suggestions and her endless support during this project. Also, I would like to thank V.R.S.S MOKKAPATI from Nanotechnology Research and Application Center (SUNUM), Sabanci Unviersity, for his technical support. Furthermore, thank you very much to all my labmates along this one year, for their support. Finally, I would like to express my appreciation to my family, my fiance Gökhan DEVECİ and his family and also Ruhsan EREYLI, Olcay EREN for their long-standing encouragements, support and sacrifice.

November 2015

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ABBREVIATIONS

CNT	**:** Carbon nanotubes
GO	**:** Graphene oxide
NMP	**:** N-Methyl-2-pyrrolidone
PVP	**:** Polyvinylpyrrolidone
SEM	**:** Scanning Electron Microscope
PS	**:** Polysulfone
RO	: Reverse osmosis
NF	: Nanofiltration
UF	: Ultrafiltration
MF	: Microfiltration
∆P	: Pressure difference
∆C	: Concentration difference
∆Y	: Electrical potential difference
∆T	: Temperature difference

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FABRICATION, CHARACTERIZATION AND ANTIBACTERIAL PERFORMANCES OF NANOCOMPOSITE POLYSULFONE MEMBRANES INCLUDING GRAPHENE OXIDE NANOPARTICULES

SUMMARY

The membrane technologies take an important places on the seperation applications. However, membrane filtration technologies have some disadvantages. One of most important disadvantage is the fouling which has negative effect on filtration performance. Biofouling is the accumulation of microorganisms, plants, algae, or animals on wetted surfaces. There are lots of articles about membrane biofouling and fouling problems. In these articles, there are three titles; the modification of membrane surface with physical and chemical treatment, and the production of membrane with adding nanomaterials which is then called nanocomposite membranes. The nanocomposite membrane studies have given the useful results. The nanoparticles (NPs) are defined as the particles having the size of 1-100 nm and they have unique magnetic, electrical, optical, mechanical and structural properties. Beside all of these properties, some nanoparticles have antibacterial properties and these antibacterial property gives the membrane high toxicity to a broad spectrum of microorganisms including bacteria, fungi, viruses. Membrane chemistry and antibacterial properties of nanoparticules can solve the most important problem in membrane systems. A membrane material among synthetic polymers that polysulfone (PS) has used in many research, its thermal and mechnical properties and chemical stability is desirable. However, it is not immune from biofouling problem and because of its hydrophobicility and charge interactions between membrane surface, it suffers more than other membrane materials. To help the biofouling problem, various approaches have been taken. Utilizing graphene oxide (GO) in preparing the membrane systems is from the unique properties that GO possesses owing to its functional groups such as carboxyl, epoxy, and hydroxylgroups on its basal planes and edges. The using of GO in membrane material would induce hydrophilicity, which would ensure high water permeation and impede biofouling owing to the low interfacial energy between a surface and water.

This work has focused on fabrication, characterization and antibacterial performances of composite polysulfone membranes which is include graphene oxide nanoparticles. The aim of this study is to examine the production of membranes with nanomaterials and the investigation of these kind of membranes at the filtration systems. All of the experiments were performed at three stages. In the first step, membrane production were done. In the second step, the membrane characterization tests were done. Finally, the antibacterial performances of fabricated bare and nanocomposite membranes were tested.

GRAFEN OKSİT NANOPARÇACIKLARINI İÇEREN NANOKOMPOZİT POLİSULFON MEMBRANLARIN ÜRETİMİ, KARAKTERİZASYONU VE ANTİBAKTERİYEL PERFORMANSLARI

ÖZET

Membranlar, ayırmanın ve taşınımın gerçekleştiği seçici geçirgen engeller olarak tanımlanabilmektedir. Membranlar polimerik, cam, metal ve sıvı materyallerden hazırlanabilirler ve gözenekli veya gözeneksiz, simetrik veya asimetrik, ya da kompozit olabilirler. Membran içerisinde bulunan küçük delikler büyük tanecikleri tutup küçük taneciklerin geçmesini sağlar. Malzemenin membranın içinden geçmeye zorlayan güç yoğunluk, basınç, elektrik veya kimyasal potansiyeldir. Membranlar yaprak, tüp, kılcal boru veya içi boş elyaflar şeklinde üretilebilir. En yaygın membranlar polimer membranlardır. Bu tür membranların ultrafiltrasyon, ters osmoz, gaz ayrıştırması ve dializ gibi çok çeşitli uygulamaları vardır.

Farklı polimerler (Polietersulfon (PES), polisülfon (PS), selüloz asetat (SA) vs.) iyi ısı direnci ve kimyasal direnci, çevresel etkilere dayanıklılık, kolay işleme ve iyi fiziksel ve kimyasal özellikleri göz önünde bulundurularak membran malzemesi olarak seçilebilir. Genel olarak membranlar ince ve daha geçirgen bir destek malzemesinin üzerinde olacak şekilde üretilirler. Bu destek malzemesi gerekli mekanik mukavemeti de sağlar. Membran materyali normal olarak termal ve kimyasal koşullara, oksitleyicilere karşı dayanıklı olmalıdır. Özellikle kimyasal olarak yıkama yapıldığında bu önemlidir. Membranların tıkanmaya karşı da dayanıklı olması gereklidir.

Membran teknolojileri ayırma uygulamalarında önemli bir yere sahiptir. Buna karşılık, membran filtrasyon teknolojileri bazı dezavantajlara sahiptir. Tıkanma, organik ve inorganik maddelerin membran yüzeyinde ve membran gözeneklerinde birikimidir. Filtrasyon performansı kaçınılmaz şekilde membran kirlenmesi nedeniyle zamanla azalır. Ancak, yapısı nedeniyle bazı polimerlerin doğal hidrofobisiteleri ve membran akıları düşüktür. Polimerler kullanılarak özel tekniklerle fiziksel ve kimyasal dayanımı yüksek membran materyalleri üretilebilir. Fakat bu materyaller genel olarak hidrofobik olup, biyoreaktördeki hidrofobik materyallerle tıkanmaya açıktır. Bu nedenle membran materyallerin yüzeyleri modifikasyona tabi tutularak hidrofilik hale getirilir.

Membran tıkanma mekanizması ve tıkanma önleyiciler hakkında birçok makale bulunmaktadır. Bu makalelerde üç ana başlık vardır; fiziksel ve kimyasal işleme ile membran yüzey modifikasyonu, nanokompozit membran olarak adlandırılan nanomalzeme içeren membran üretimidir. Nanokompozit membran çalışmaları yararlı sonuçlar vermiştir.

Grafen iki boyutlu, bir atom kalınlığında elmasta ve grafitte olduğu gibi bir karbon alotropudur. Grafen sp^2 bağlı karbon atomlarından oluşmuştur ve atomları arasında 0.142 nm molekül bağ uzaklığı vardır. Karbon atomlarının iki boyutlu altıgen bir yapıda dizilmiş bu formu, doğada iki boyutlu tek malzeme örneğini oluşturmasının

yanı sıra, grafene birçok değişik özellik kazandırmaktadır. Atomları çok sıkı bir şekilde dizilmiştir. Buna rağmen grafen kolayca esneyebilir ve değişik formlardaki bir çok malzemenin yüzeyine kolayca kaplanabilir. Grafenin en önemli üç özelliği çelikten 100 ile 300 kat arası daha sağlam olması, şu ana kadarki bilinen oda sıcaklığında en iyi iletken olması ve esnek olmasıdır. Grafen bilinen en ince ve en hafif malzemedir ve saydamdır. Bir grafen tabakası küresel halde yuvarlandığında fulleren, silindir şekli verildiğinde ise karbon nanotüp oluşturur. Grafen'e oksijen atomları eklenerek elde edilen grafen oksit çok güçlü ve esnektir.

Grafen oksitteki carbon katmanları polimer matrisiyle birleştiğinde düşük konsantrasyonlarda bile polimerin fiziksel özelliklerini önemli ölçüde etkiler. Grafen oksitin seçilmesinin nedeni hidrofilikliği ve pH duyarlılığıdır. Bunun yanı sıra çaışmalar gösteriyor ki GO negatif yüzey yüküne sebep olur. Bunların yanı sıra GO bulunduğu polimerin mekanik dayanıklılığınıda arttırmaktadır. GO in yüzeyinde bulunan çeşitli hidrophilik fonksiyonel gruplar dolayısı ile suyu kolayca emer.

Bu çalışmanın temel amacı nanomalzemeler ile membran üretimi ve karakterizasyon deneylerinin ardından antibakteriyel performanslarının belirlenmesidir. Bu tez çalışmasında evre dönüşümü yöntemi ile grafen nanoparçacıkları kullanılarak tabaka halinde olarak adlandırılan membranlar üretilmiş ve sonrasında bu membranların karakterizasyonu ve antibakteriyel performanslarına bakılmıştır. Bu çalışma kapsamında dört (4) farklı konsantrasyonda grafen oksit nanoparçacıklı çözelti ve polimer olarak polisülfon kullanılarak membran üretimi gerçekleştirilmiştir. Bu nedenle saf membranda dahil olmak üzere toplamda beş (5) farklı grafen oksit konsantrasyonlarında membran üretilmiştir. Bu çalışma iki ana başlık altında özetlenebilir;(i) evre dönüşüm yönteminde, saf polimerik membranların hazırlanması ve farklı grafen oksit konsantrasyonu ile üretilmesidir, (ii) ilk aşamada üretilen farklı konsantrasyonlara sahip membranların antibakteriyel performanslarının tespit edilmesidir.

Deneylerin ilk aşamasında membranların hazırlanması için sabit PVP (%8) membranlar hazırlanmıştır. Nanomateryalli membran üretiminde dört (4) faklı GO oranı kullanılmıştır. Her bir nanomateriyal için kullanılan nanomateriyal oranları % 0.009-0.012-0.024-0.049 olarak seçilmişdir.

Düz plaka halinde saf polimerli membranların dökümünde evre dönüşüm (phase inversion) yöntemi kullanılmıştır ve membranların döküm işlemleri aynı şartlar altında gerçekleştirilmiştir. Membran dökümünde ilk olarak homojen dağılımı sağlanmış membran çözeltisi cam yüzey üzerine belirli hacimde dökülmüş ve dökme bıçağı (casting knife) sabit kalınlığa ayarlanarak bu çözeltinin üzerine yerleştirilmiştir ve cam yüzeyinde polimer film oluşturulmuştur. Ardından polimer filmlerinin olduğu camlar değişik konsantrasyonlarda grafen oksit çözeltisi bulunan ve homojenliğin sağlanması için içerisine mikser daldırılmış koagülasyon banyosuna daldırılmışlardır, membranın oluşması beklenmiş ve ardından oluşan membranlar distile suyla dolu kaba alınmıştır. Biyolojik büyümenin olmaması için üretilen membranlar $+4^0$C"de soğuk odada saklanmışlardır.

İkinci aşama olan karakterizasyon deneylerinde karakterizasyon deneylerinde manyetik karıştırmalı klasik filtrasyon hücresi kullanılarak geçirgenlik deneyleri yapılmıştır. Cihazlar kullanılarak yapılan karakterizasyon ölçümlerinde, temas açısı, SEM, yüzey yükü, gözeneklilik, yüzey pürüzlülüğü, dayanıklılık, elastisite modulü analizleri gerçekleştirilmiştir. İlk olarak bu membranlar litaratürde de sıkıştırma olarak adlandırılan geçirgenlik öncesi yapılan bir işleme tabii tutulmuştur. Sıkıştırma

işlemi;yüksek basınç uygulanarakmembranların saf su ile yıkanması ve bu esnada reaksiyona girmemiş madde kalıntılarının membranlardan yıkanması ve membran gözeneklerinin son halini almasıdır. Ön işlem olarak sayılan sıkıştırma işleminden sonra filtrasyon deneyleri sırayla gerçekleştirilmiştir. Diğer karakterizasyon kısmı olan cihaz analizleri için membran numunelerinin hazırlanmasında sıkıştırma ön işlemi yapılmayan membranlar kullanılmıştır. Membranların por çaplarına bakılmış ve fiziksel deformasyon hakkında bilgi veren çekilme deneyi yapılmıştır. Membranların yüzeylerinin hidrofilik veya hidrofobik özelliğin ölçümü için kullanılan temas açısı cihazında damlatma yöntemi ile analizler tekrarlı olarak yapılmıştır. Sonrasında ise membranların yüzey özellikleri için SEM cihazı ve yüzey pürüzlülük sonuçları için ise optic profilometre cihazı kullanılmıştır.

Çalışmanın son kısıma gelindiğinde *E.coli* bakterisi ile çalışmalar yapılmıştır. Son kısım olarak değerlendirilen bu kısımda membran yüzeylerinde tıkanmaya neden olabilecek mikrobiyal bir üreme olup olmadığının tespiti için agar-plateler kullanılmıştır. Gerçekleştirilen bütün bu aşamalardan sonra antibakteriyel performansı yüksek olan optimum nanokompozit membranlar belirlenmiştir.

1. INTRODUCTION

Water is the foundation of all of life. However, population is increasing and water scarcity become a very important problem in all over the world. However, to solve this problem membrane technologies is expected to play very important role in water treatment. Especially, polymeric membranes is mostly using in water treatment processes because of their higher flexibility and lower costs than other inorganic membranes. Some researchers take an inerest in polymer–matrix nanocomposite membranes due to their very attractive properties such as unique mechanical, electrical, optical and thermal properties. Because of nanomaterials performances, they can be used in membranes which is used in environmental applications. Mebrane processes properties and efficiency can be controlled by the chosing proper polymer, solvents, or some other materials like nanoparticles using in nanocomposite polymeric membranes. Membran fouling which can be defined as the accumulation of particles, salt molecules, organics, inorganics at the membrane surface and inside of the membranes. In membrane processes, the fouling is a serious problem for all membrane processes such as reverse osmosis (RO), nanofiltration (NF), ultrafiltration (UF), and microfiltration (MF). The membrane fouling causes the decreasing membrane performance and a higher energy use, a higher cleaning frequency. Especially, biofouling is known as 'Achilled heel' of the membrane process because microorganisms can be grow up even if almost all are removed, there are still enough cells remaing and they can continue to multiply and it is a contributing factor to all membrane fouling but it is a major problem in nanofiltration (NF) and reverse osmosis (RO) membrane filtration. Antibacterial agents are used to improve the antibiofouling properties of membranes by improving or optimizing the membrane surface properties. Fabricating composite membranes is the most widely used approach. Nanomaterials are new "functional material" in membrane modification area. They can be either blended in the matrix membrane or coated on the membrane surface. Nanomaterials could give the membrane excellent anti-biofouling and antibacterial properties.

1.1 Purpose of Thesis

The purpose of this study is to investigate the production of nanocomposite membranes with nanomaterials (graphene oxide), characterization of them and examination of their antibacterial properties. This study was carried out same polymer but graphene oxide nanoparticles which is in different concentrations and the purpose is to see optimum nanomaterial concentration in the membrane matrix. The experiments is carried out with membrane characterization, filtration and antibacterial tests which is provided the determination of the best-performing type of nanocomposite membranes.

1.2 Scope of Thesis

In this thesis work, the experiments were performed at three stages. Firstly, the graphene oxide composite membranes were fabricated. Secondly, the bare and nanocomposite membranes were characterized. Finally, the antibacterial performances of fabricated bare and nanocomposite membranes were tested. As a result of this thesis, newly synthesized nanocomposite membrane materials contributed to literature for membrane fabrication studies.

2. LITERATURE REVIEW

2.1 Nanomaterials

Nanotechnology is a very important area of science that involves the engineering of nanosize particles of various materials. According to U. S. Environmental Protection Agency (EPA), nanotechnology can be defined as 'the creation and use of structures, devices, and systems that have novel properties and functions because of their small size.' (Khare et al., 2014). In the nanoscale world, everything is different from in the macroscopic world. At sub- microscopic levels, objects have properties of quantum mechanics laws (Adams and Barbante, 2013). Therefore, nanoparticles have different optical, magnetic or electrical properties than bulk particles. These properties have potential to be used in a wide range of areas such as in energy production and storage, materials, medicine, information technologies, manufacturing and environmental applications (Holister et al., 2003).

There are three (3) ways to reduced dimensions based on bottom-up and top-down approaches or self-assembly. At top-down nanofabrication, is produced nanometer scale devices from bulk materials by lithography techniques (Adams and Barbante, 2013).

2.1.1 Physical and chemical properties of nanomaterials

At the nanoscale, materials have unique characteristics different from the same material when compared to large scale. Melting point and dielectric constant known as specific properties, but the situation changes in nanoscale. This change is known as the "size effect." Nanoparticles show a number of unique characteristics in their morphological, structural, thermal, electromagnetic, optical, and mechanical properties (Loos, 2015).

The elevated specific surface area of nanoparticles affects their reactivity and solubility. When the atoms located on the surface of the particles are influenced by the nanoscale, the melting point of the nanoparticles decreases as compared to the same materials on a large scale. At nanoscale, electromagnetic properties also changes, for

example gold nanoparticles exhibit unique catalytic characteristics, unlike the gold which is stable at normal scale. As the size of certain particles reaches the nanoscale, the absorption of light starts to take place at a specific wavelength different from that observed when the same material was on a large scale. The hardness of crystalline materials generally increases with decreasing size of the crystals and the mechanical strength of these materials is high (Loos, 2015).

2.1.2 Application areas

Nanotechnology is known as an interdisciplinary area. This interdisciplinary area and the nanoparticle applications are discussed here.

Nanotechnology can be used in microelectronics for circuits, sensors, displays, coatings, energy applications for solar cells, fuel cells etc., and in environmental applications (Freddy at al., 2013).

Some of nanoparticles are used in medicine industry such as quantum dots (QD), particles with interesting optical and electronic properties, are able to selectively bind to cancer cells and mark them.

One of the other application of nanotechnology is the construction of micro- and nano-robots that could be programmed to repair specific diseased cells. Also, nanotechnology can be used in food industry. Reinforced clay nanocomposites are used in bottles, packages, and films to obtaining impermeable barriers to gases such as oxygen, carbon dioxide, or moisture.

Nanotechnology can be used in energy area for power generation using fuel cells. For example, using platinum have higher costs than using in nanometer size because the using of platinum nanoparticles reduces the amount of material needed due to a large increase in the surface area. The addition of nanoparticles or nanofibers to fabrics also can improve its properties without increasing weight, thickness of these materials (Loos, 2015).

Nanotechnology is now being used to develop solutions for different problems related to environmental problems (Loos, 2015). For example, adsorption, membranes and membrane processes, photocatalysis, disinfection and microbial control, sensing and monitoring are the applications of using nanotechnology in water and wastewater treatment (Qu et al., 2013).

2.2 Membrane Systems

A membrane can be permeable or semi-permeable phase, polymer, inorganic or metal. Figure 2.1 shows the fundamentals of membrane. This membrane controls the relative rates of transport of various species through itself and thus, gives one product depleted in certain components and a second product concentrated in these components.

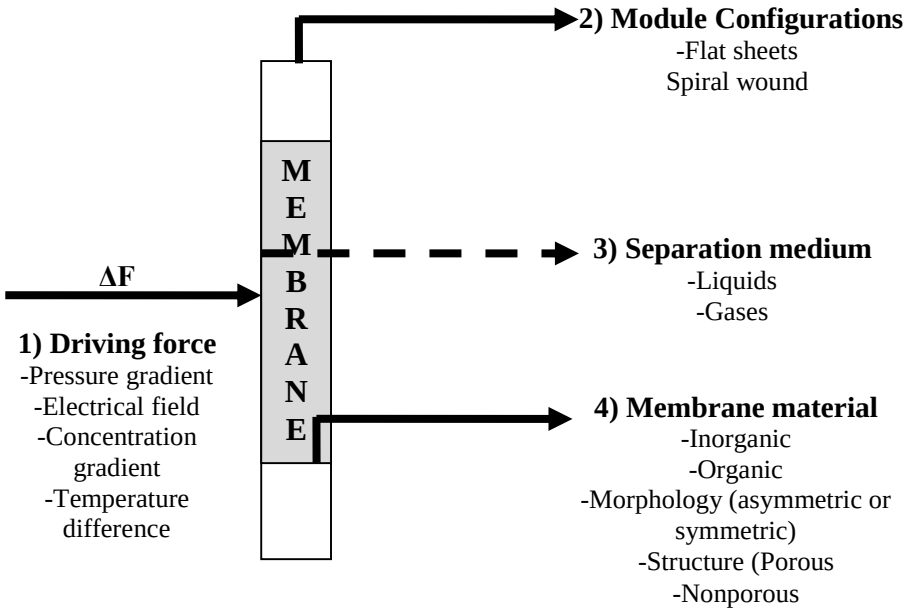


Figure 2.1 : Fundamentals of membrane and membrane processes.

Membranes are used for the separation of mixtures of gases and vapours, miscible liquids and solid/ liquid and liquid/liquid dispersions and dissolved solids and solutes from liquids (K. Scott, 1995). Membrane separation processes can be used for a wide range of applications and can offer significant advantages over conventional separation (Cui et al., 2010). Transport of selected species from somewhere through the membrane can be achieved by applying a driving force to the membrane (K. Scott, 1995).

Membrane processes are using in many different area in the world. Especially, the membrane technology now using in water and wastewater treatment technologies. Membrane processes can be classified according to their type of material which the membrane is made, the nature of driving force, the separation mechanism, and the

nominal size of the separation achieved showed by a diagram in Figure 2.2 (Tchobanoglous and George, 2003).

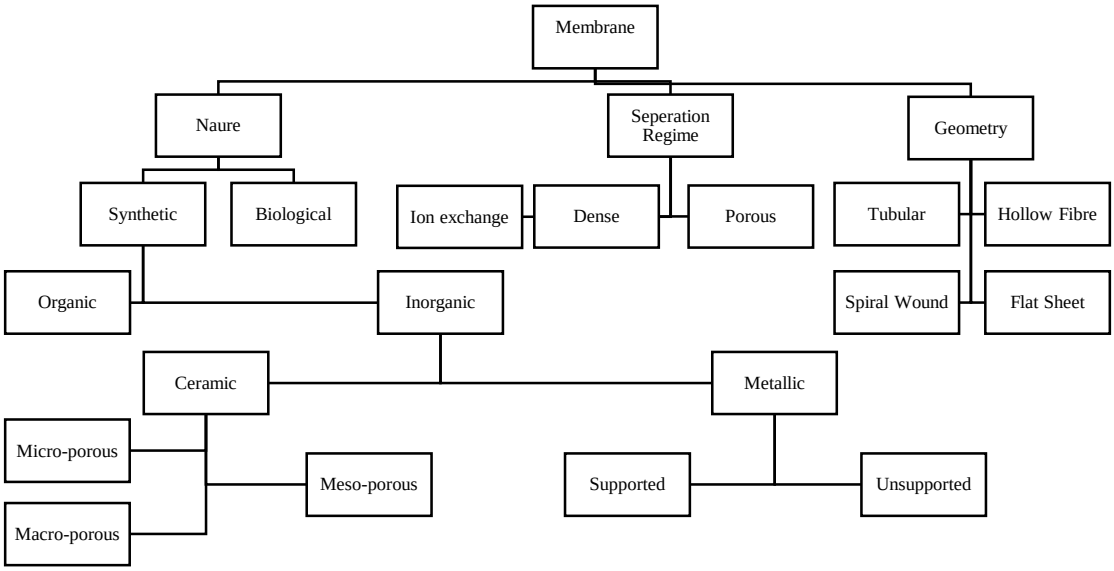


Figure 2.2 : Membrane classification.

Membranes can be natural, synthetic, neutral or charged. The first classification is by nature. They can be nature,biological or synthetic membrane. Synthetic membranes can be divided into organic (polymeric,liquid) and inorganic membranes (ceramic,metal) (Mulder, 1996).

Synthetic membranes show a large variety in the materials which they are made from also in their physical structure. They can classified as porous membranes, homogeneous solid membranes, solid membranes carrying electrical charges and liquid or solid films containing selective carriers. Moreover, the structure may be symmetric or asymmetric. Membrane materials can be polymers, ceramics, metals also the membrane configuration can be flat, tubular or hollow fiber. In a symmetric membrane, the structure and the transport properties are identical over the entire cross section and the thickness of the entire membrane and it determines the flux. Symmetric membranes can be porous or dense. As functionality and structure, symmetric microporous membrane resembles to commercial filters. The difference from commercial filters is having very small pores that are between 0.01 to 1 micrometer in diameter (Baker, 2004).

Membranes can also classify as porous or nonporous. Porous membranes enable separation by differentiation between particle sizes. These membranes are used in microfiltration and ultrafiltration. Membranes can be highly selective when the pore size is greatly smaller than solute size (Mulder, 1996). Particles larger than the largest pore of the membrane rejected and smaller particles than largest pore of membrane are relatively rejected depend on the distribution of membrane's pore size. Also, much smaller particles than smallest pore of the membrane traverse the membrane. Therefore, microporous membrane's separation of solutes depend on molecular size. Nonporous membrane compromise of a dense film. Dense membranes are used for mostly gas separation, RO (reverse osmosis) and pervaporition membranes for separation. Another symmetric membrane type is electrically charged membranes that can be found as microporous or dense but principally they are microporous which have positively or negatively charges ions on pore walls. A membrane with positively charges ions are an anion-exchange membrane that binds anions from fluid.

Asymmetric structure means that the pores are wider and farther away from the surface, which prevents the pores from being plugged. This property provides good fouling resistance (Wagner, 2011).

The driving force can be either pressure, concentration, temperature or electrical potential. Classification in terms of suspended solids, colloids or dissolved solutes, etc is preferred. The techniques of microfiltration, ultrafiltration, is in the category of suspended solid separation. All of them use membranes which are microporous in nature. These are the most simplest form of membrane regarding mode of separation and consist of a solid matrix with defined pores ranging from 100 nm to 50 micron in size (K. Scott, 1995)

Driving force of reverse osmosis (RO), nanofiltration (NF), ultrafiltration (UF) an microfiltration (MF) membranes is pressure (ΔP) shown as in Figure 2.3. Pervaporation and dialysis membranes' driving force is concentration (ΔC). Electrodialysis and electrodialysis reversal membranes driving force is electrical potential (ΔY). Also there are membranes which the driving force is temperature (ΔT) (Drioli and Giorno, 2010).

RO, NF and UF membranes are asymmetric. MF membranes have 5 to 0.1 micron, UF membrane have 0.1 to 0.01 micron and NF, RO membranes have 0.001 micron pore size. Pores have not been observed in RO an NF membranes using a microscope, water can pass through the membrane and salt is rejected (Wagner, 2011).

Inorganic materials have good chemical and thermal stability but their uses as membrane are limited. Four different types of inorganic materials are ceramic, glass, or metallic membranes. Metallic membranes obtained by sintering of powders. Ceramic membranes are prepared by sol-gel processes (Mulder, 1996).

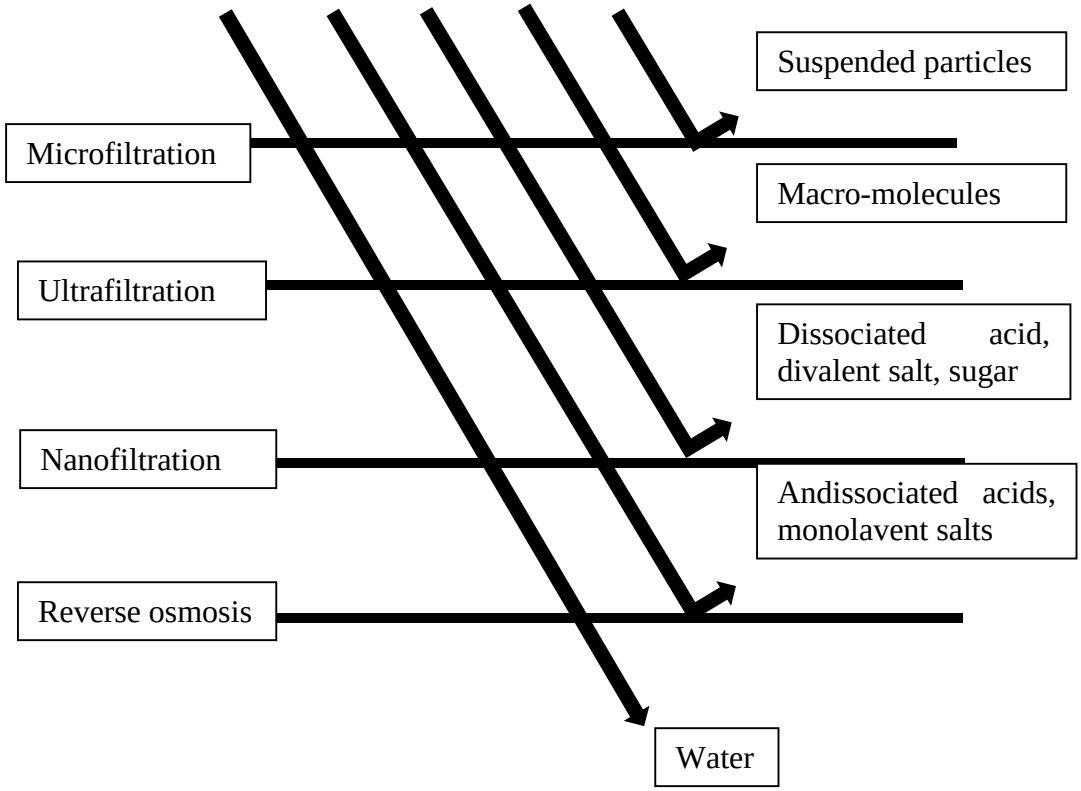


Figure 2.3 : Pressure driven membranes for water and wastewater treatment.

2.3 Membrane Polymers

All polymers can be used as barrier or membrane material but the chemical and physical properties differ so much and it is a limited factor be used in practice (Mulder, 1996).

2.3.1 Polysulfone

Polysulfone is often preferred because of its desirable thermal and mechanical properties, and also its chemical stability but it is not immune from the biofouling problem. In fact, it suffers more than the other membrane materials due to hydrophobic and charge interactions between membrane surface and diverse foulants (Lee et al., 2013).

Polysulfone membranes are used in MF and UF membranes. Polysulfone is characterized by having in its structure diphenylene sulfone repeating units. The SO_2 group in the polymeric sulfone is stable. Repeating phenylene rings produce high rigidity, strength, creep resistance, dimensional stability, and heat deflection temperature. Phenyl ether and phenyl sulfone groups have high thermal and oxidative stability, and also they produce longterm, high temperature stability during use. Polysulfone membranes have wide temperature limits, wide pH tolerances. Polysulfone has good chlorine resistance and it is easy to fabricate in wide range of pore sizes available in MF and UF applications. Also, they have good chemical resistance to alcohols and acids but not much resistance to ketons,esters. However, polysulfones hydrophobicity, making it prone to fouling in comporasion to the more hydrophilic polymers. Polysulfones are the apparent low pressure limits (Chervan, 1998).

2.3.2 Other membrane polymers

Celluloseacetate (CA) is known as original membrane and is can be used for RO, NF and UF applications but it has a number of limitations, mostly with respect to pH and temperature. The main advantage of CA is its low price, and also it is hydrophilic. However, CA can be eaten by microorganisms. Polyvinylidenedifluoride (PVDF) is a traditional membrane material, but it is difficult to make membranes. Its main advantage is its high resistance to hydrocarbons and oxidizing environments (Mebrane filtration handbook, 2001). Aromatic polyamides (PA), are membranes that can be used at high temperature and have the characteristics of high resistance to organic solvents. They are characterized by the amide (-CONH-) linkage in structure. Thay cope with many disadvantage of cellulose acetate membranes (such as pH and temperature influence), but the resistance to chlorine species is worse than cellulosic

membranes. Chlorine increase the selectivity and reduces the permeability of the membrane by damaging the the aromatic rings of polyamide (Nath, 2008).

Hydrophobic materials such as poly(vinylidene fluoride) (PVDF) and isotactic polypropylene (PP) are often used for microfiltration membranes. Poly(vinylidene fluoride) (PVDF) membranes are made from phese inversion. Polypropylene (PP) is a good solvent resistant polymer and they can be prepared by stretching and phese inversion. Polyacrylonite (PAN) is a polymer which is used for ultrafiltration membranes (Mulder, 1996).

Polycarbonate is a transparent thermoplastic and it has good mechanical strength and can be used in making UF and MF membranes by phase inversion. Polyacrylonitrile processes are resistant to oxidation and used to prepare UF and porous supports of composite membranes (Basile, 2015).

2.4 Membrane Production Techniques

There are several different techniques to prepare synthetic membranes. Some of them are possible to use to prepare both organic or inorganic membranes. The most important techniques are sintering, stretching, track-etching, phase inversion (Mulder, 1996).

2.4.1 Sintering

Sintering is simple technique to obtain porous structures. A powder is pressed into a film and sintered below the melting point. Sintered membranes can be made on a large scale from ceramic materials such as aluminum oxides, graphite. To determine the pore sizes of the final membrane, the particle size of the powder is must be considered. Particle size of the powder determine the lower limit of the pore diameter. They are also suitable for gas separation. (Drioli and Giorno, 2010).

2.4.2 Strectching

Stretching is also a simple procedure for preparing porous membranes. This technique is employed with films of polyethylene. The crystalline in the semicrystaline polymer are aligned in the direction of drawing. After annealing and cooling processes, the extruded film is stretched perpendicular to the direction of drawing and doing this

leads to a partial fracture of the film and uniform pores are obtained (Drioli and Giorno, 2010).

2.4.3 Track etching

In track etching, a film is exposed to high energy particle radiation adopted perpendicular to the film and polymer matrix is devastated by the particles to cause tracks. Then to create uniform cylindrical pores with narrow pore size distribution the film is immersed in an acid or alkaline bath and along these tracks the polymeric material is etched (Mulder, 1996).

2.4.4 Template leaching

Template leaching is to produce porous microfiltration membranes. These membranes are often have a narrow pore size distribution and high fluxes. The procesess is also applied to prepare membranes from glass, metal alloys. In the preperation procedure for porous glass and metal membranes, two different types of glass or metal are mixed, then one type is dissolved and a network with well defined pore sizes of the undissolved material is obtained (Drioli and Giorno, 2010).

2.4.5 Phase Inversion

Phase inversion process is the most important methods to prepare asymmetric membrane. Polymeric membranes are produced by phase inversion, an exchange process between liquid and solid phase (Mohanty, 2012). Phase inversion technique include very different techniques such as precipitation by controlled evaporation, thermal precipitation from the vapour phase and immersion precipitation (Mulder, 1996).

The Loeb–Sourirajan technique is known as the phase inversion process. In all phase separation processes, a liquid polymer solution is precipitated into two phases: a solid, polymer-rich phase that forms the matrix of the membrane and a liquid, polymer-poor phase that forms the membrane pores. This technique was discovered by Loeb and Sourirajan. In first Loeb–Sourirajan process, a solution containing 20 to 25 wt% cellulose acetate dissolved in a water-miscible. This process is part of the membrane preparation procedure for reverse osmosis and ultrafiltration and for many gas separation membranes. This procedure is used in the laboratory but not for the commercial purpose.

The polymer–solvent–precipitation medium phase diagrams popularized by Michaels, Strathmann and Smolders. In this approach the change in composition of the casting solution as membrane formation look like is tracked as a path. The path starts at a point known the original casting solution and finishes at a point the composition of the final membrane. The casting solution composition go thorough to the final membrane composition by losing solvent and gaining water. The figure shows the typical three-component phase diagram for the components used to prepare Loeb–Sourirajan membranes.

The triangle in Figure 2.4 shows three pure components, these are polymer, solvent, and nonsolvent (water); points within the triangle represent mixtures of the three components.

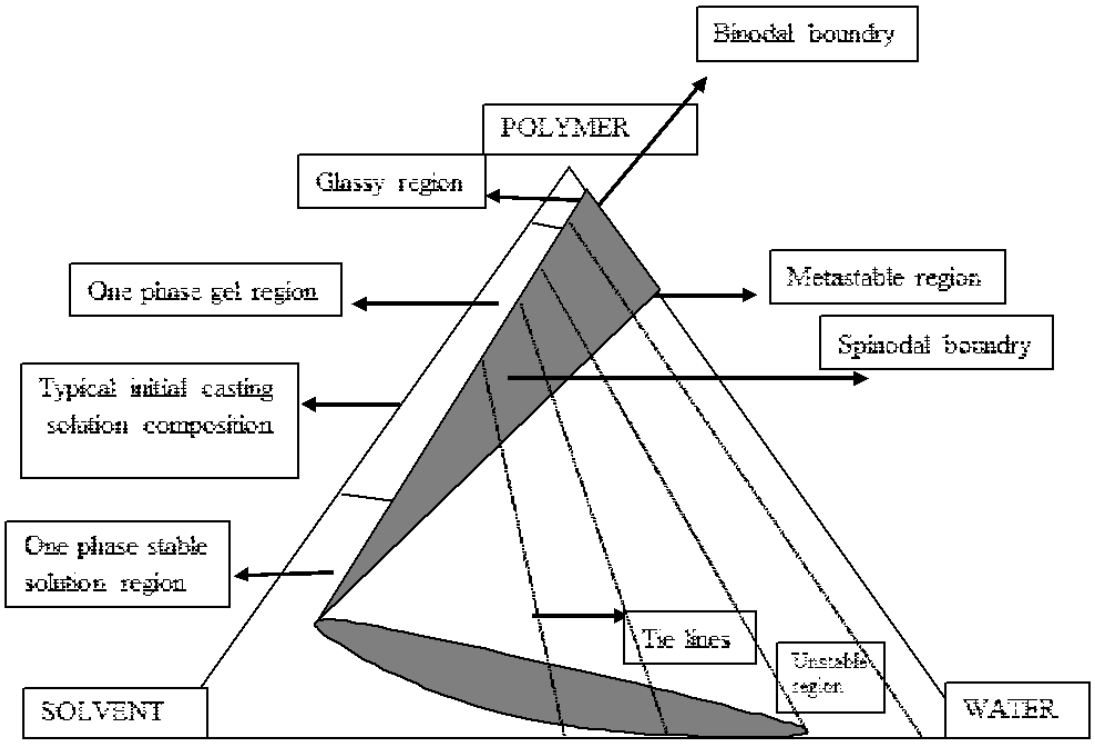


Figure 2.4 : Schematic of the three-component phase diagram.

There is two principal regions in the diagram: a one-phase region, all components are miscible; and a two-phase region, the system separates into a solid (polymer-rich) phase and a liquid (polymer-poor) phase. During precipitation of the membrane casting solution, the solution loses solvent and it gains water. The casting solution go through from a composition in the one-phase region to a composition in the two-phase region. The one-phase region is thermodynamically continuous, but for practical purposes it can be subdivided into a liquid polymer solution region, a polymer gel region, and a

glassy solid polymer region. Because of this, in the low-polymer-concentration region, the compositions are viscous liquids. But, if the concentration of polymer is increased, the viscosity of compositions in the one-phase region increases rapidly and the system can be seen as a solid gel. The transition between the liquid and gel regions is arbitrary but can be placed at a polymer concentration of 30 to 40 wt%. On the other hand, if the one-phase solution contains more than 90 wt% polymer, the swollen polymer gel may become so rigid and the polymer chains can no longer rotate. After this, the polymer gel becomes a solid polymer glass. During the precipitation process, the casting solution enters the two-phase region of the phase diagram by crossing the binodal boundary. This situation brings the casting solution into a metastable two-phase region. In this area, polymer solution compositions are thermodynamically unstable. The metastable region in the phase diagrams of low-molecular-weight materials is very small, but it can be different for high-molecular-weight materials. During, more solvent leaves the casting solution and water enters the solution, the composition crosses into another region of the phase diagram. In this region a one-phase solution is always thermodynamically unstable and polymer solutions separate into two phases with compositions linked by tie lines in here. The boundary between the metastable and unstable regions is known as the spinodal boundary. Thus, this process that is called membrane precipitation process has series of steps. First, solvent exchange with the precipitation medium starts, then, phase precipitation begins. The time to first precipitation may be almost as long as 30–60 s and it depens on the casting solution composition. At this point, the polymer phase may be a liquid or semi-liquid gel, and the precipitation domains may be able to flow and agglomerate. At the end of the precipitation process, desolvation of the polymer phase converts the polymer to a solid gel phase, and the membrane structure is fixed. The solid polymer phase forms the matrix of the final membrane, and the liquid solvent–nonsolvent phase also forms the pores (Baker, 2004).

2.5 Membrane Modification Methods

To increase the overall performance of the membrane, membrane modification is required. The main objective of membrane modification are to increase flux, selectivity, and chemical resistance (Lawrence, 2011). Nanocomposite membranes can be modify by blending them with polymeric or inorganic membranes (Bottino et al.,

2002) or by assembling engineered nanoparticles into porous membranes (Li et al., 2009a; Kim et al., 2003; Taurozzi et al., 2008).

2.5.1 Plasma treatment

Plasma treatment is a technique which membrane modification is to expose the surface of a membrane to plasma. In this process, plasma exposure causes in a more hydrophilic membrane surface. Plasma treatment has the advantages of the increased fouling resistance of modified membranes (Xu and Zhi-Kang, 2009).

2.5.2 Graft polymerization

Physically graft an additional poymer onto the surface of membrane is an another modification technique. Polymer is typically hydrophilic, and it causes a given membrane that is hydrophobic to become more hydrophilic. The main purpose of this type of modification technique is to create a membrane with highly hydrophilic surface while maintaining the flux and seperation characteristics. Moreover increasing hydrophilicity can increase the mass transfer coefficient, and membrane becomes more efficient (Xu and Zhi-Kang, 2009).

2.5.3 Photochemical membrane polymerization

This technique uses monomers which are photochemically sensitive and, when the monomer distributed onto the membrane, it is exposed to ultraviolet radiation at various wavelengths. The exposure to UV induces the photochemically sensitive polymers to polymerize onto to membrane surface, it becomes part of the modified membrane (Xu and Zhi-Kang, 2009).

2.5.4 Blending

The mixing polymers is very easy and cost effective method of modifying various properties of a polymer such as fexibility, and processability. Property of polymer blend may be directly related to compatibility or miscibility of polymers forming a blend. Thermodynamic incompatibility between polymers usually causes demixing of polymers to occur. When the polymer is equilibrated in air, hydrophobic polymer will concentrate at the air interface and reduce the systems interfacial tension.

2.5.5 Coating

Coating is a very simple process. Hydrophilic, biocompatible materials are physically deposited on the membrane surface via adsorption/adhesion, interpenetration by mixing between the added functional material and the base polymer in an interphase and mechanical interpenetration of an added material layer and the pore structure of the membrane. By doing one of these, the surface property of the membrane could change from hydrophobic or non-biocompatible to hydrophilic and biocompatible but this method cannot gain a stable surface, for the materials absorbed on the membrane surface run away easily (Xu and Zhi-Kang, 2009).

2.5.6 Self-assembly

In nature, self-assembly occurs. Many complex systems can formed by self-assembly. In this technique, there are self-assembled monolayers (SAMs) and layer-by-layer (LBL) assembly, which is a new technique for membrane surface engineering. SAMs are ordered molecular assemblies formed by the adsorption of an active surfactant on a solid surface and when system approaches the equilibrium, the order in these two-dimensional systems is produced by a spontaneous chemical synthesis at interface (Xu and Zhi-Kang, 2009).

2.6 Nanoparticles for Membrane Fabrication

Production of nanocomposite membranes by adding,blending,coating nanoparticles to polymers provide desired structured membranes and high controlable over biofouling mechanisms,antibacterial properties (Li et al., 2009b; Cortalezzi et al., 2002, 2003).

2.6.1 Carbon nanotubes (CNT)

CNTs have capability to separation characterics (Goh and Ng, 2013). CNTs are composed of cylindrical graphite sheets (allotropic formof carbon) rolled up in a tube. While single-walled carbon nanotubes (SWCNTs) have cylindrical shape consisting of a single shell of graphene, multi-walled carbonnanotubes (MWCNTs) are composed of multiple layers of graphene sheets (Das et al., 2014).

2.6.2 Graphene sheet

Graphene is one-atom-thick 2D sheets, consisting of sp^2 bonded carbon atoms arranged in a hexagonal, honeycomb lattice. They have specific surface area, high thermal conductivity and excellent electrical conductivity. The most important property of graphene is its extremely versatile and tunable carbon backbone, and this properties leads to facile functionalization, and incorporation in a variety of applications (Mahmoud et al., 2015).

2.6.3 Graphene oxide

Graphite oxide have stacked graphene layers which have been decorated with oxygen-containing functional groups, such as hydroxy, epoxy, and carboxylic acids. GO is decorated with various oxygen-containing functional groups, its 2D lattice is highly defective, and this property makes it electrically insulating, unlike pristine graphene, which is highly conducting. The oxygen-containing groups on GO reduce its conductivity, but they also allow GO to be suspended in aqueous solutions and make it labile to a variety of chemical reactions, which may be used to control its resulting properties. Water solubility provides GO to be compatible with biorelated applications that are not accessible to graphene, because it is not soluble in water and must be supported on a substrate (Galande et al., 2014).

GO membrane allows unimpeded permeation of water but their work does not ruled out the joint propagation of organic molecules dissolved in water through GO membrane. Graphene does not allow anything to pass through. Graphene oxide (GO) has excellent membrane characteristic and offer huge potential for real membrane applications (Joshi et al., 2015).

GO may have various groups, such as epoxide, hydroxyl, carbonyl, and carboxyl groups. These oxygen functional groups on GO provide facile dispersion in aqueous mediums without the need for surfactants or stabilizing agents. They also allow for a variety of surface-modifications, which can be used to develop a series of functionalized GO-based membranes with superior separation performance. Nanopores can be introduced into GO sheets to allow for water permeation when other unwanted ionic substances rejected. These functional nanopores provide to GO sheets with the capacity for selective sieving, improve water flux, and enhance properties

such as antifouling. Structural defects of GO sheets provide primary passages for water transport across the stacked GO nanosheets (Khaled et al., 2015).

2.7 Antibacterial Membrane Fabrication

Biofouling means the the accumulation of microorganisms, plants, algae, or animals on wetted surfaces (Wikipedia, 2015). Biofouling causes to reduction of the performance of membranes, the biodegradation of the membrane material, and increase in the power consumption due to the necessity to raise the operating pressure (Kochkodan et.al., 2006). The development of new membrane material reduces these high costs. Thus, it is necessary to improve the characteristics of membranes via surface coating, surface grafting and blending (Liu et.al., 2009).

Antimicrobial membranes have high filtration efficiencies and they are resistant to biofouling. Metal elements such as silver, copper, zinc, nickel, manganese can improve the antimicrobial properties. Some of metals have been blended with polymers. Silver nanoparticles have very strong antimicrobial nature. Sometimes, the addition of antimicrobial additives can also influence the morphology and diameter of nanofibers and the filtration capabilities. The change in conductivity and viscosity of the polymer solution due to the additives are very important parameters, because they can affect the outcome of the end product (P.N.L.Lens et al., 2013).

3. EXPERIMENTAL METHOD

3.1 Materials

Brands and product codes of solvent(s), polymer(s) and the nanomaterials are shown in Table 3. 1. Chemicals are used without extra purification.

Table 3. 1 : Brands and product codes of materials used for the experiment.

Chemical Name	Brand	Code
Polysulfon (PS, Mw=10000 Da)	BASF	Ultrason S6010
Polyvinylpyrrolidone(PVP,Mw=10000 Da)	Sigma-Aldrich	PVP10
1-Methyl-2-pyrrolidinone (NMP)	Sigma-Aldrich	328634
Graphene oxide (0.5 to 5 microns)	Graphene supermarket	HC
Eosin Methylene Blue Agar	Merck Millipore	101347
LB Broth	Merck Millipore	71753

3.2 Preparation of the Membrane Solutions

3.2.1 Preparation of the membrane (dope) solutions with bare polymer

For the preparation of bare polymer solutions, the ratio of materials are determined according to the weight percentage (% weight). For PS polymer, NMP is used as a solvent.

Images of the dope solution preparation process (for bare membranes) are shown in Figure 3.1 : In the first step of solution preparation, PVP is added to the solvent and stirred for 20 min with a magnetic stirrer until it is completely dissolved. PS dope solution is prepared at room temperatures. After the PVP is completely dissolved in the solvent, polymer is added and stirred with a magnetic stirrer for 24 h in order to obtain homogeneous solutions. Solution is kept in an ultrasonic bath for 20 h before membrane preparation.

Figure 3.1 : Dope solution preparation steps for pure membranes.

Graphene oxide is used as nanomaterial. Graphene oxide solutions was obtained by Graphene Supermarket,and its properties are listed in Table 3. 2.

Table 3. 2 : Graphe oxide properties.

Material	Concentration (g/L)	Composition (%)	Flake size(μ)	Thickness	Color
Graphene Oxide (175 ml)	5	Carbon-79 Oxygen-20	0.5-5	1 atomic layer	Brown

Nanomaterial, polymer, PVP and solvent ratios for the preparation of nanomaterial containing dope solutions are PS-16 %, PVP10-8 %, NMP-76 %, and nanomaterial ratios are adjusted as GO-0.009-0.012-0.024-0.049 %.

3.3.2 Fabrication processes of the flat sheet membranes

Phase inversion method is used to prepare the polymer, nanomaterial containing flat sheet membranes. Images of the membrane preparation by using phase inversion method are shown in the Figure 3.2. Nanomaterial containing membrane preparation

and bare membrane preparation processes were carried out under the same conditions. In the first step, a specific volume (Figure 3.2– a) of homogeneous dope solution was poured on a glass surface and an aluminum casting knife which was arranged to a constant thickness (Sheen branded) was put on that solution (Figure 3.2– b and c). Then the laboratory scaled automatic film applicator machine in the National Membrane Technologies Research Center (MEMTEK) was adjusted to a constant velocity (100 mm/s) and a thin film was formed on the glass surface (Figure 3.2-d). In the next step, solvent was evaporated from the polymer films for a specific time interval, in order to obtain the desired properties for produced membranes (Figure 3.2-e). Evaporation time was set to 10 seconds for this step. After the evaporation process, polymer film coated glasses were put in a distilled water containing coagulation bath for bare membrane (Figure 3.2-f) and graphene oxide solution containing coagulation bath for nanocomposite membranes with mixer in the bath (Figure 3.3). Polymer film coated glasses were kept in the coagulation bath for 5 min for membrane production. Then, the produced membranes were transformed into a clean medium filled with distilled water (Figure 3.2-g and h). Produced membranes were kept in a cold room at $+4^0$C for one week to prevent the biological growth and to eliminate the unreacted polymer and solvent. The mechanism of membrane preparation by using phase inversion method are shown in the Figure 3.3.

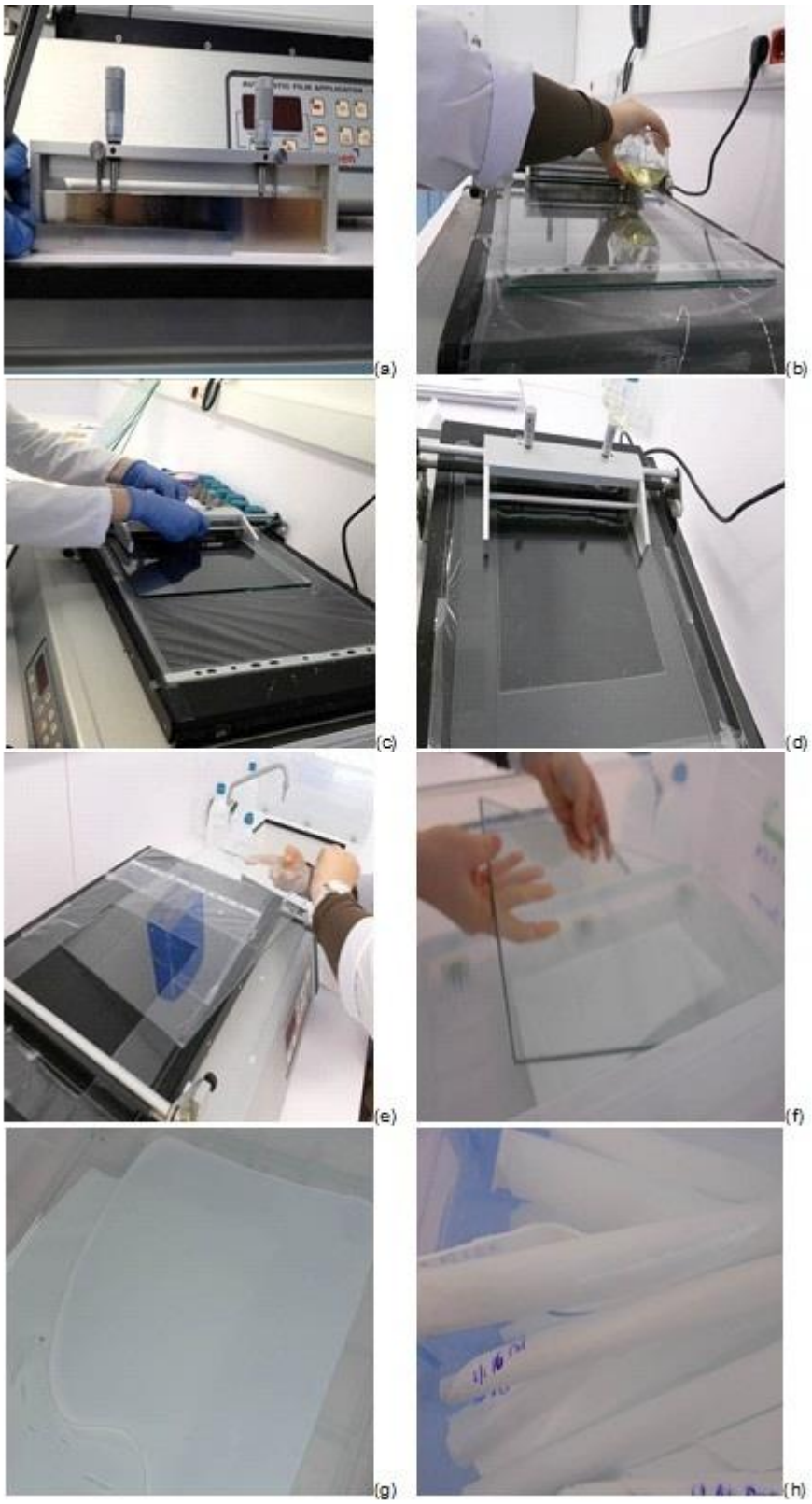


Figure 3.2 : Preparation processes of the flat sheet membranes.

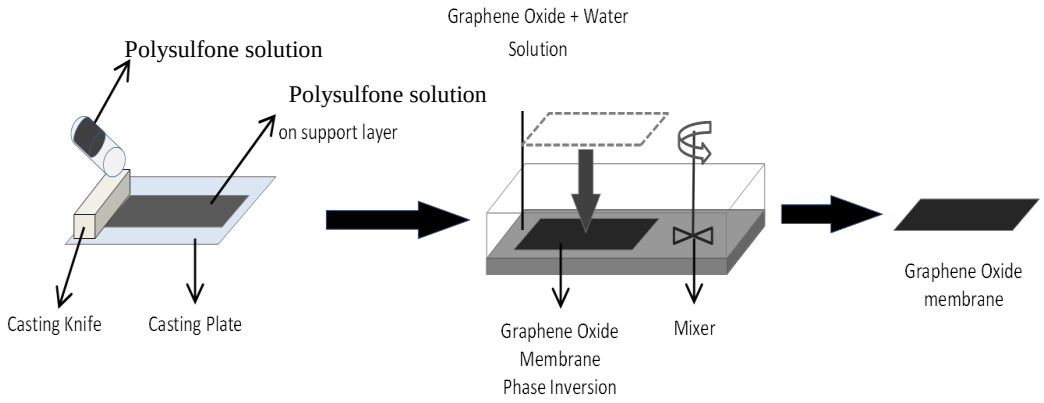


Figure 3.3 : The fabrication process GO membrane with probe mixing in bath.

3.4 Membrane Characterization Techniques

Characterization experiments of the bare and nanocomposite membranes were done after keeping the membranes for 1 week in the cold room.

Sterlitech HP4750 branded, magnetic stirrer containing classical filtration cell was used for the characterization experiments to determine permeability. Instrumental analysis such as membrane porosity and young modulus determination, contact angle, SEM, surface charge (zeta potential in the pH range of 6.0 – 6.5) and optic profilometer measurements are explained below in details.

3.4.1 Filtration system

As stated above, Sterlitech HP4750 branded magnetic stirrer containing classical filtration cell was used for the filtration experiments. Pressure in the device was adjusted by using nitrogen gas while the cross flow on the membrane surface was provided by stirring. Properties of the filtration system are indicated in the Table 3.3 as stated by the producer company.

Table 3. 3 : Technical properties of the filtration system.

Parameter	**Value**
Membrane diameter	49 mm
Active membrane area	14.6 cm^2
Volume	300 ml
Maximum pressure	69 bar
Maximum temperature	121^0C

Preparation steps of the filtration process are shown in the Figure 3.4. Experiments in the filtration cell are explained below in details.

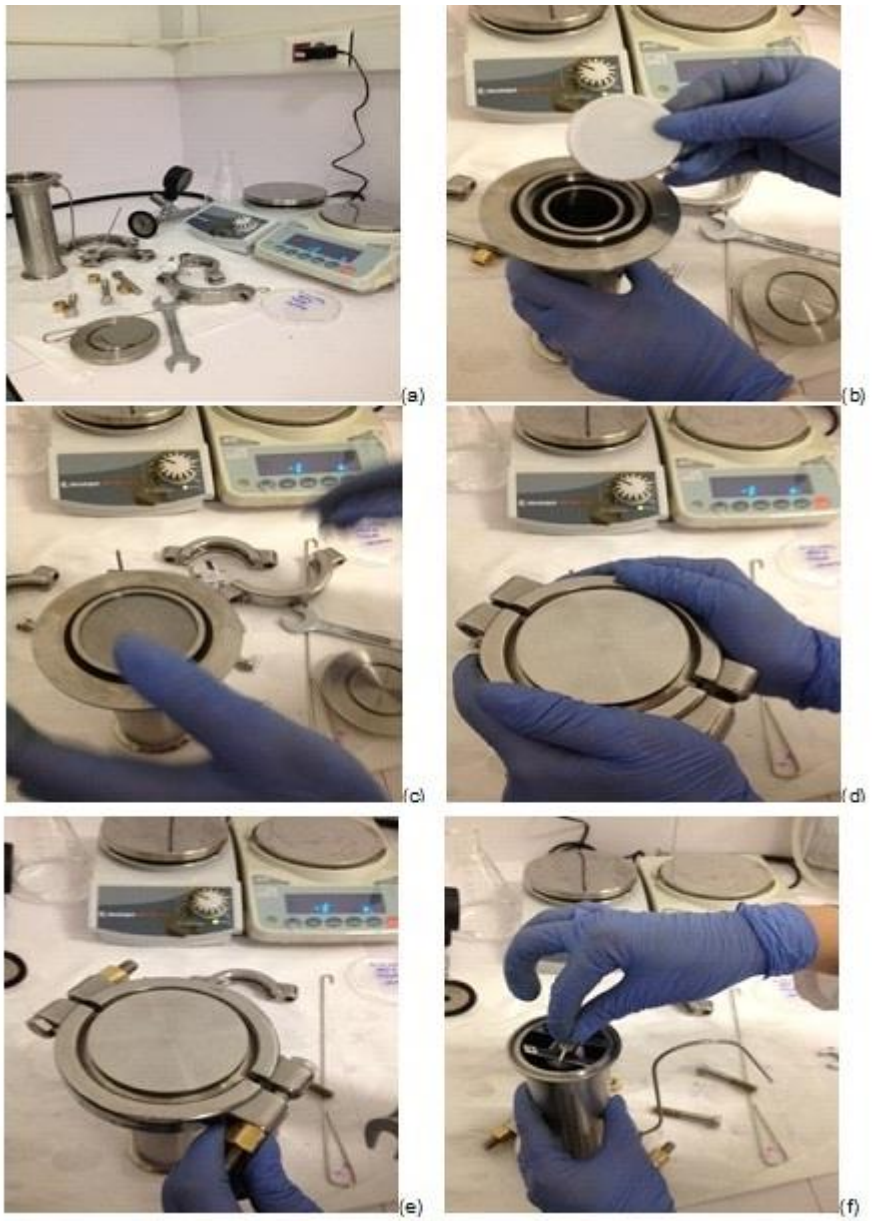


Figure 3.4 : Preparation of the filtration cell.

3.4.2 Calculation of the permeability value

Permeability values (R) of the membranes are defined as the amount of water passing through per unit area in a unit time and under a unit pressure. Calculation is done by using the equation **(3.1)** below;

$$R = \frac{J}{\Delta P} \quad \textbf{(3.1)}$$

R: Permeability, L/m^2h.bar

J: Flux, L/m^2h

ΔP: Pressure, bar

A process called compaction with distilated water filtration under high pressure, is applied to the membranes for at least 1 h to clean the membranes and to open the pores before the permeability experiment. In this process, membrane was put in a filtration cell that is filled with approximately 300 ml distilled water. Then pressure was set to a certain amount and water flow was provided for at least 1 h. Flux rates were not recorded for this process. Then, distilled water was added again to the cell and filtration was carried out for 10 min under 3 different pressure values. Flux rates for every pressure value were recorded while this process.

Afterwards, pressure – flux Graph was drawn by using Microsoft Excel and a line equation was obtained. Slope of the line shows the permeability value for the membrane. Same procedure is repeated at least 3 times for the membrane pieces obtained from the different parts of the membrane sheet and permeability values were calculated separately. Thereby, mean values of the permeability were obtained for every membrane and results could be given with mean values and standard deviation.

3.4.3 Contact angle measurements

Hydrophobicity and hydrophilicity properties that shows the wettability of the membranes were measured by using Theta model contact angle device (obtained from KSV Attension Company) in the National Membrane Technologies Research Center (MEMTEK). Measurements were done by using the sessile drop technique. Images of the device and sample preparation process are shown in Figure 3.5. Contact angles were measured for at least three membranes and the mean results were indicated with the standard deviation values.

Figure 3.5 : Contact angle measurement device and the sample preparation process.

3.4.4 Dynamic mechanical analysis

Dynamic Mechanical Analysis (DMA) determines elastic modulus, viscous modulus and damping coefficient as a function of temperature, frequency or time. The test specimen is clamped between the movable and stationary fixtures. The Analyzer applies torsional oscillation to the test sample. Dynamic Mechanical Spectrometer DMS6100 was used to examine mechanical properties of graphene oxide membranes. DMA device is shown in the Figure 3.6.

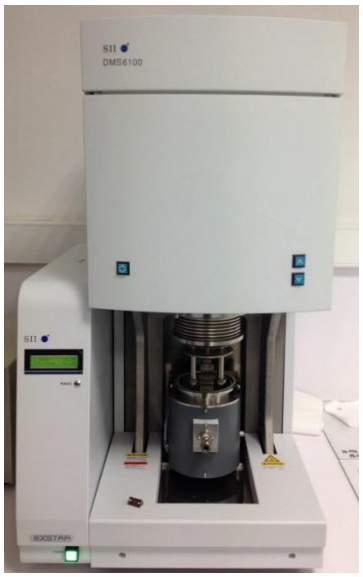


Figure 3.6 : Dynamic mechanical analyser.

3.4.5 SEM and optic profilometre measurements

Quanta Feg250 model SEM device (obtained from the FEI Company) was used to examine the surface properties of membranes in the National Membrane Technologies Research Centre (MEMTEK). And surface roughness values were determined in the National Membrane Technologies Research Centre (MEMTEK) with a NewView 7100 3D Optical Surface Profiler device. SEM device is shown in the Figure 3.7. and optic profilometer device is shown in the Figure 3.8. Samples were washed with ethanol and dried at room temperature before the analysis. Samples were coated with gold before the SEM analysis.

Figure 3.7 : SEM device.

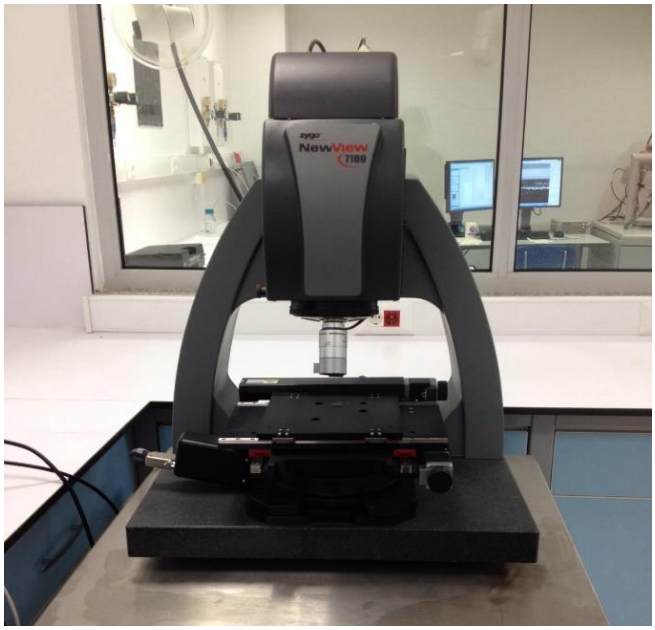


Figure 3.8 : Optic profilometer analyser.

3.4.6 Measurement of the surface charge

Surface charge of bare and nanoparticle containing membranes were measured with Surpass model electrokinetic analyzer (obtained from Anto Paar company), in the Prof. Dr. Dinçer Topacık National Membrane Technologies Research Center (MEMTEK). The device is shown in the Figure 3.9. pH was kept constant (in the 6.0-6.5 pH range) for the measurements by using KCl buffer solution. Working principle of the device relies on the mutual zeta potential measurement of the membrane pieces which were set on two interfaces.

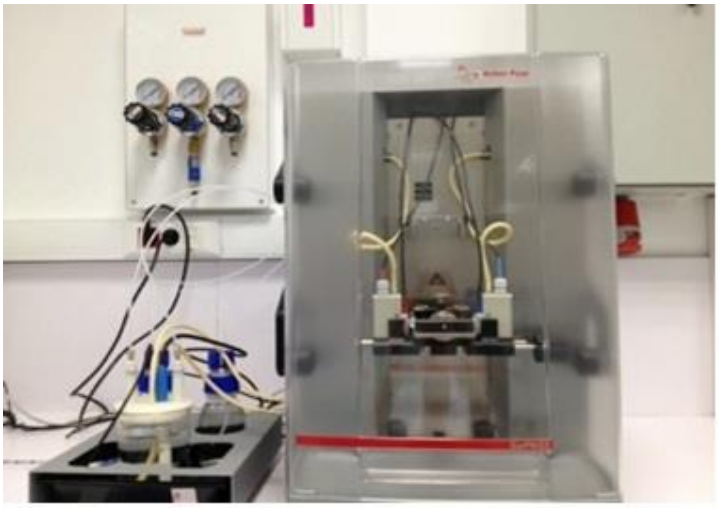


Figure 3.9 : Surface charge measurement device.

3.4.7 Measurement of Fourier transform infrared spectroscopy (FTIR)

Fourier transform infrared spectroscopy (FTIR) is a technique which is used to obtain an infrared spectrum of absorption or emission of a solid, liquid or gas (Wikipedia, 2016). FTIR used in this study to see the functional groups on the membrane surface. Perkin Elmer labeled FTIR device can be seen in Figure 3.10.

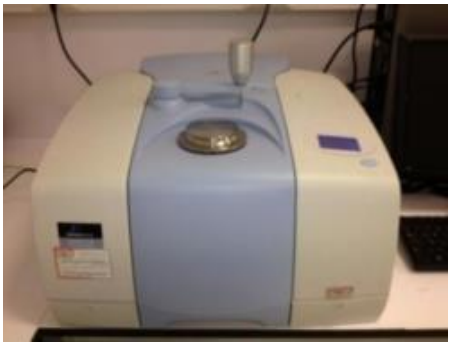


Figure 3.10 : Fourier transform infrared spectroscopy (FTIR).

3.5 *E.coli* Experiment

Experiment were applied under sterile conditions in order to examine the biological contamination of membranes by using a *Escherichia coli* (*E.coli*) strain and a filtration cell. *Escherichia coli* (*E.coli*) strain was obtained from Istanbul University ÇAPA Faculty of Medicine, Microorganism Culture Collections Research and Application Center (KÜKENS). First step was the preparation of *E.coli* suspension. Bacteria culture (as powder) was put in a liquid bacterial growth medium and spread on an agar-containing plate. Incubation temperature was 37ºC for all growth media. Sterile growth media and sterile agar-containing plates were used for the experiments. Used tools were also sterilized by using a bunsen spirit burner for this process with under necessary precautions. Regulations and steps for using lyophilizate ampoule are indicated below;

• Information written on the ampoule should be noted on a notebook.

• A cutt line should be marked 2.5-3 cm below the top of the ampoule with an ampoule cutter.

• Ampoule should be held with an alcohol containing cotton and vicinity of the cutt line should be decontaminated.

• Ampoule should be broken by holding with alcohol containing cottons from both sides.

• Top of the ampoule should be put in a disinfectant containing medium.

• Cutting edge of the ampoule must be closed with a piece of cotton.

• 0.2 cm^3 Liquid broth should be added to the ampoule by using a Pasteur pipette.

• Inoculation should be done in the liquid broth from suspension and in the solid medium by using serial dilution method.

Proliferation of Bacteria: After the dry and inactive organisms were activated in the growth media, they were proliferated according to the procedures on different plates in order to obtain required number of organisms for the experiments. Process was carried out under sterilized conditions. Used glass materials were kept in an autoclave for a while. Petri dishes and pipettes were obtained as sterilized. Metal materials were incandesced by using a Bunsen spirit burner and cooled again before using.

Figure 3.11 : Images of the E.coli inoculation and enumeration processes.

Preparation of the liquid broth and solid growth medium: Determination of the amount and proliferation of the bacteria were required. Thus, obtained pure cultures were inoculated to the liquid broth and solid growth medium. Images of the inoculation and enumeration process are shown in Figure 3.11.

Prescription for solid growth medium (500 mL);

- 5 g Tripton
- 2.5 g yeast

- 18 g bactoagar
- 5 g NaCl

Chemicals were weighted and put to the autoclaved sterile solution dish in an order. After it was diluted to 500 mL, solution was heated and stirred. Growth medium was then autoclaved. Top of the plate was left partially open while keeping it in the autoclave. Autoclaving process was carried out under 121^0C and 1.06 bar pressure. A OT032 model, vacuum drier included, tabletop, steam-power sterilizer device (obtained from Nuve company) was used as the autoclave. Since agar-containing growth mediums freeze at room temperatures, temperature of the solution was controlled at certain time intervals to prevent freezing of agar-containing growth mediums and applied to the plates at 40-45^0C. Bacteria which were activated in the liquid broth were applied to the agar and kept at a cold room after preliferation. Solutions were prepared with the density of $2x10^7$ bacteria/mL by using these bacteria to be used for the antibacterial experiments. *E.coli* solutions were prepared and same solution was applied to every membrane.

4. EXPERIMENTAL RESULTS

4.1 Permeability Values of the Membranes

Permeability tests were applied for at least 3 times to the first set of membranes produced by using same amounts of bare polymers, different amount of graphene oxide and a certain amount of PVP.

Results of the tests are shown in Table 4.1. Permeability of the PS nanocomposite membranes are measured as; 118±0.07 L/m^{2}h.bar for bare membrane, 123±1.13 L/m^{2}h.bar for G0-0.009%, 158±18.6 L/m^{2}h.bar for G0-0.012%, 98±13.8 L/m^{2}h.bar for G0-0.024%, 142±0.8 L/m^{2}h.bar for G0-0.049%. As can be seen from the results, produced G0-0.012% graphene oxide membranes have the highest permeability values.

Table 4 .1 : Permeability of bare and GO membranes.

Membrane type	**Permeability (L/m^{2}h.bar)**
PS	118±0.07
G0-0.009%	123±1.13
G0-0.012%	158±18.6
G0-0.024%	98±13.8
G0-0.049%	142±0.8

CNTs and graphene oxide are nanoparticles which can improve the all parameters like permeability, pore size, contact angle etc. (Liu et al., 2013). Xia and Ni, showed that different concentrated graphene oxide membranes (0.0, 0.1, 0.5, and 1.0 wt%. PVDF) permeability did not increase with increasing GO content. The purewater flux was highest when the amount of GO was 0.50 wt%, while the higher concentration of 1.0 wt% GO led to decrease in the flux (Xia and Ni, 2015). In this study, also permeability value increased and then decreased. Addition of GO loading significantly increased the pure water permeability to 158 L/m^{2}h.bar. However, further increase in GO loading to reduced the water flux. It is known that enhancement of surface hydrophilicity due

to GO addition could facilitate easier permeation of water through the support. The permeability results are shown in Figure 4.1.

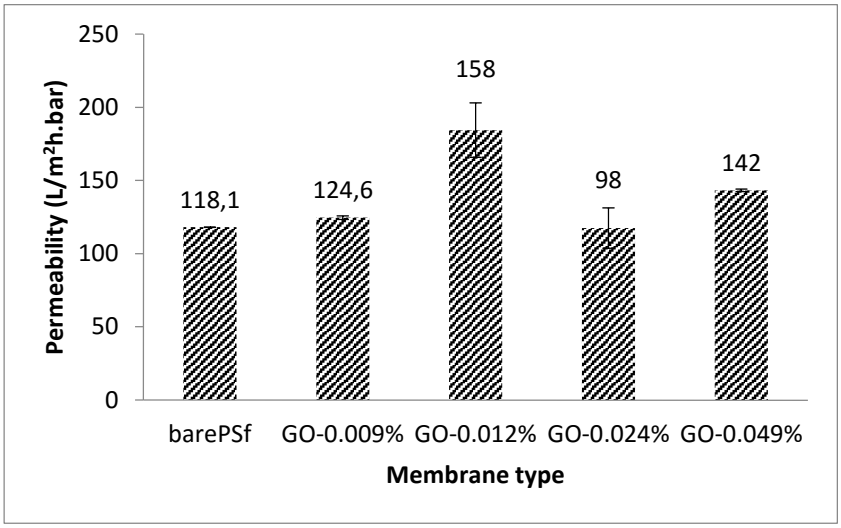


Figure 4.1 : Permeability values of the bare and GO membranes.

4.2 Pore size of the Membranes

The pore size of a membrane gives mean size of the pores on a membrane surface. It can range from 1000 to 0.0001 microns and there are four types of membranes; Microfiltration (MF), Ultrafiltration (UF), Nanofiltrations (NF) and Reverse Osmosis (RO). UF membranes reject particles such as silica, viruses, endotoxins, proteins, plastics. In this study, the pore sizes show that the GO composite membranes are Ultrafiltration (UF) membrane. Pore size measurement results are given in Table 4.2.

Table 4 .2 : Pore sizes of bare and nanomaterial contining membranes.

Membrane type	**Pore size (µm)**
PS	0.031
G0-0.009%	0.029
G0-0.012%	0.031
G0-0.024%	0.035
G0-0.049%	0.034

Based on the mean pore radius, the results are presented in Figure 4.2 , the mean pore radius of the membranes was almost same around G0-0.009% and G0-0.012% concentration and then increased. This behavior is similar to the way that water passed through the membranes. Generally, pore size is tend to increase.

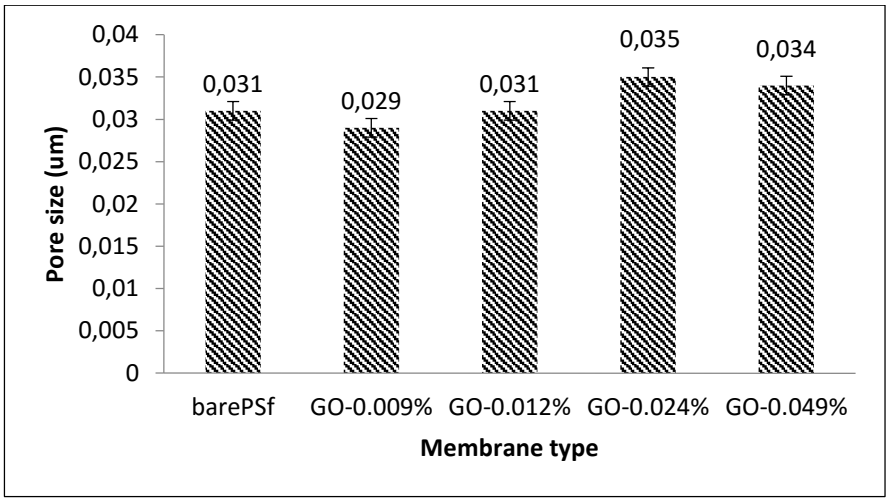


Figure 4.2 : The results of pore size measurements.

4.3 Contact Angle Results

Contact angles of the produced bare and nanocomposite polymeric membranes were measured in order to examine the hydrophilicity and hydrophobicity properties after drying process. Measured contact angle values are given in Table 4.3.

Table 4 .3 : The results of contact angle of GO membranes

Membrane type	**(°)**
PS	72±5°
G0-0.009%	42±9°
G0-0.012%	44±8°
G0-0.024%	64±6°
G0-0.049%	71±5°

Nanoparticle addition make the membrane surface hydrophilic. In the higher concentration, GO was remained in bottom of the membrane and cause the surface hydrophilicity is almost same with PS and in the lower concentration contact angle decreased and give to the membrane more hydrophilic properties like in the most of the membranes. Generally, the smaller contact angle, the greater is the hydrophilicity. C.Zahao et al., showed that the additive amount of GO was increased, which indicated that the surface hydrophilicity was improved with the increase of GO content in membranes.

Large amount of –OH groups of the GO nanosheets dispersed on the surface could be responsible for the hydrophilicity increasing. However, in our study while the additive amount of GO was increased, surface hydrophilicity was not improved, it decreased with the increase of GO content in membranes. In the lower concentration, GO was remained in upper part of the membrane and because of this surface hydrophiliciy is higher than lower GO concentration membranes. The contact angle results are shown in Figure 4.3.

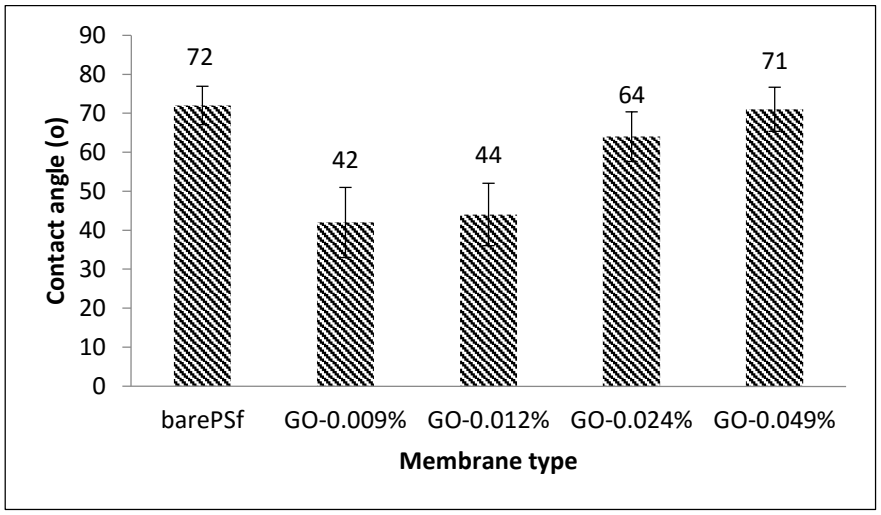


Figure 4.3 : Measured contact angles of the GO polymeric membranes.

4.4 Results of the Surface Charge Measurements

Surface charge is one of the most important surface parameters of a substance, and plays important roles in the interfacial interactions and membrane fouling in MBRs. (Cai et al., 2016). Moreover, GO has different functional groups attached to its surface which are responsible for surface charge and eventually imparts surface charge to membrane. The dissociation of carboxylic group attached to graphitic back bone and dissociation of phenolic groups. These are responsible for the production of surface charge. They cause negatively charged ions which interact with water through ion-dipole interaction that leads to increased water uptake (Ganesh et al., 2013).

Measured surface charge values of the bare and nanomaterial containing polymeric membranes are given values as a graph in Figure 4.4. Surface charge measurements were done for all membranes. As can be seen from Figure 4.4. lowest surface charge values were obtained for the PS membranes having nanoparticles G0-0.012%, highest

surface charge values were obtained for the PS membranes having nanoparticles G0-0.049% .

The ionization of oxygen groups leads to a high stability of GO aqueous dispersion. Considering the case of GO platelets, the interparticle interaction is completely based on the charge stabilization and double layer extension (Jzwang et al., 2013).

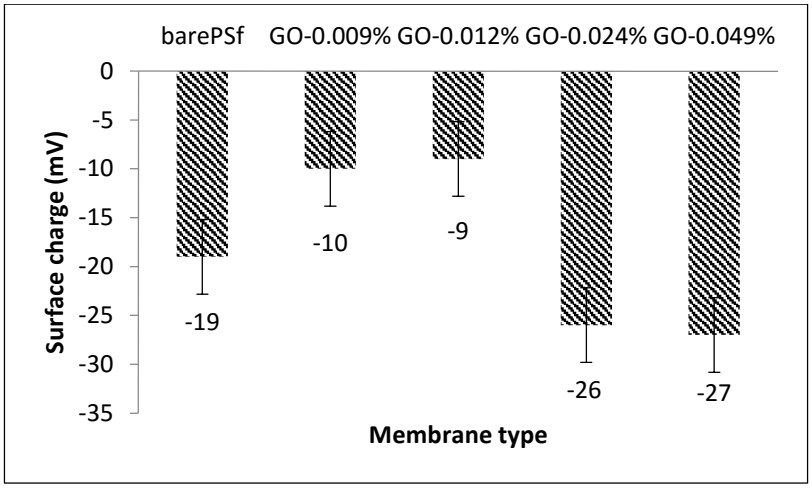


Figure 4.4 : Measured surface charge values of the bare and nanomaterial containing polymeric membranes.

4.5 Result of Dynamic Mechanical Analysis

Young's modulus or elastic modulus, is a mechanical property of linear elastic solid materials. It defines the relationship between stress (force per unit area) and strain (proportional deformation) in a material A solid body deforms when a load is applied to it. If the material is elastic, the body returns to its original shape after the load is removed. The material is linear if the ratio of load to deformation remains constant during the loading process. (Wikipedia, 2015).

Nanoparticles like carbon nanotube, graphene oxide can have an improved tensile strength than the pristine membranes (Liu et al., 2013). Young module values of analysed membranes are changing between 1.67×10^{10}– 4.26×10^{10} Pa. Consequently, adding GO to the polymer matrix increased the mechanical strenght as shown in Figure 4.5.

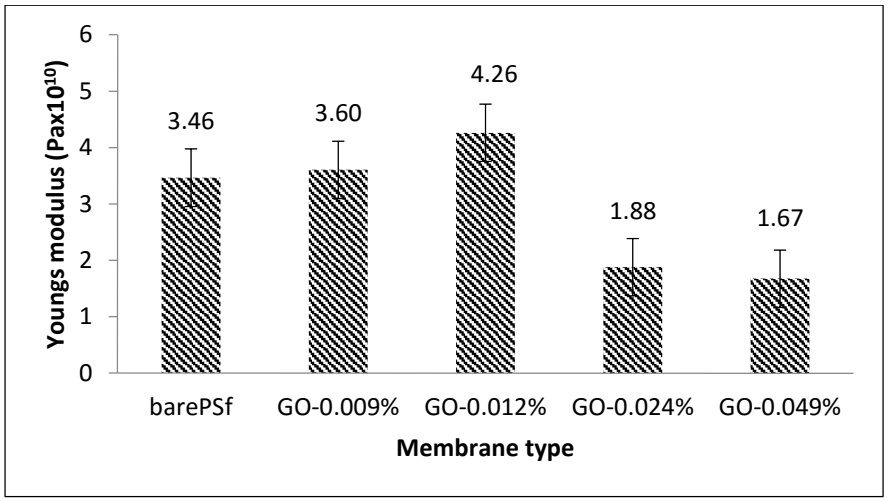


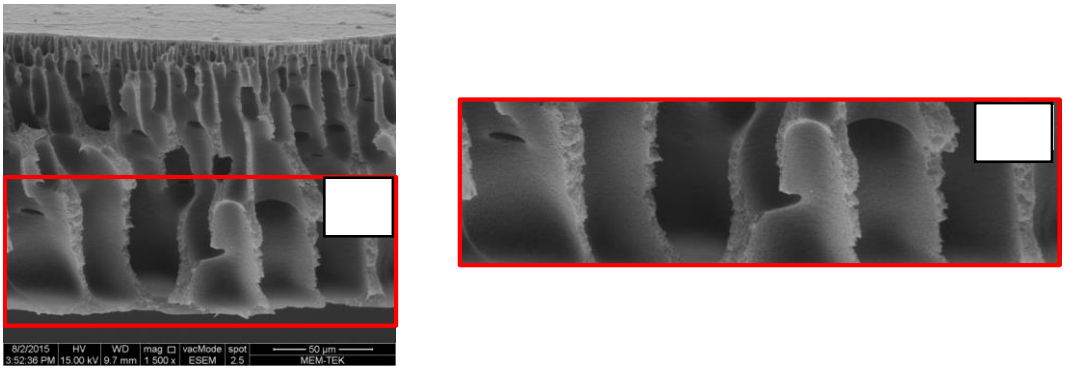
Figure 4.5 : Measured young modulus values of the bare and nanomaterial containing polymeric membranes.

On the other hand, increasing the amount of GO to G0-0.049% led to weaker mechanical strength due to aggregation of GO in the PS matrix. As a result, mechanical strength of membrane added G0-0.012% concentration is higher than other membranes.

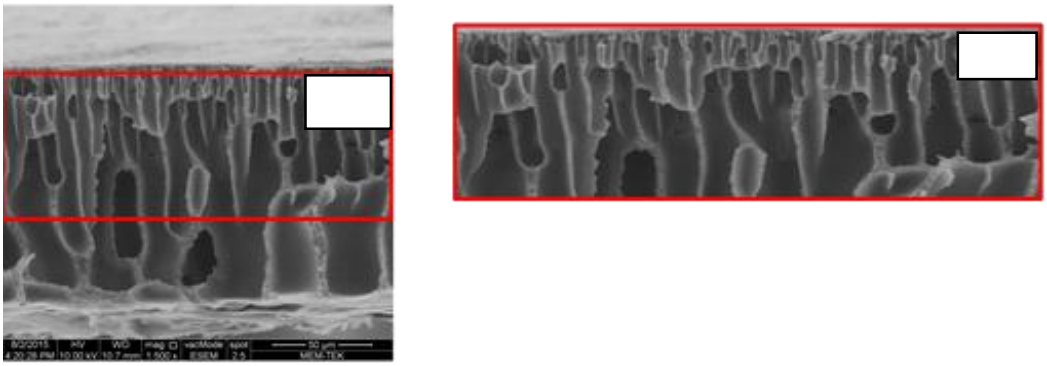
4.6 Sem and Optic Profilometer Analysis

4.6.1 SEM analysis

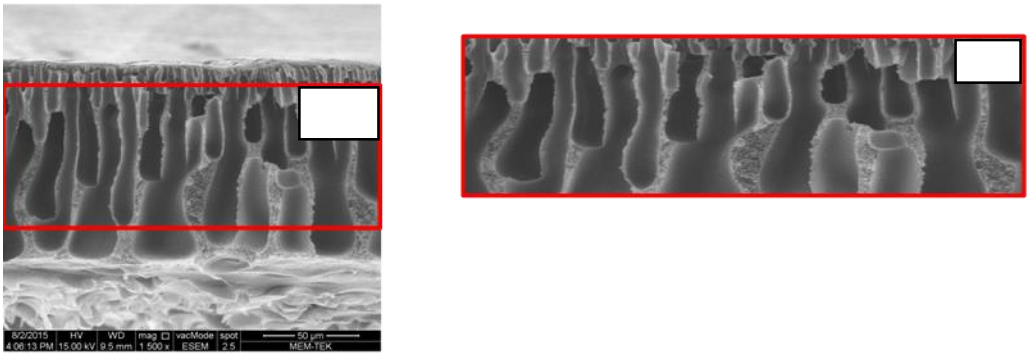
Images obtained from the SEM analysis results of bare and nanomaterial containing membranes are shown in Figure 4.6. SEM analysis were done for the 16% polymer containing bare PS membrane, and for the % 0.009-0.012-0.024-0.049 nanomaterial containing PS membranes for further comparison.



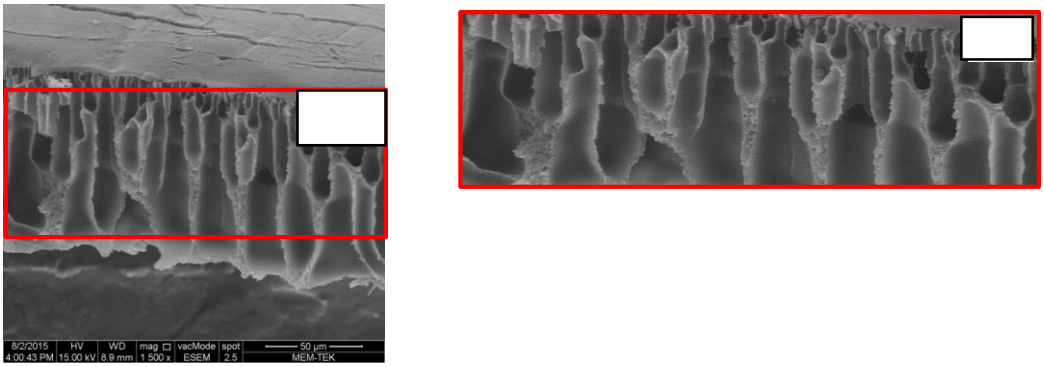
a)



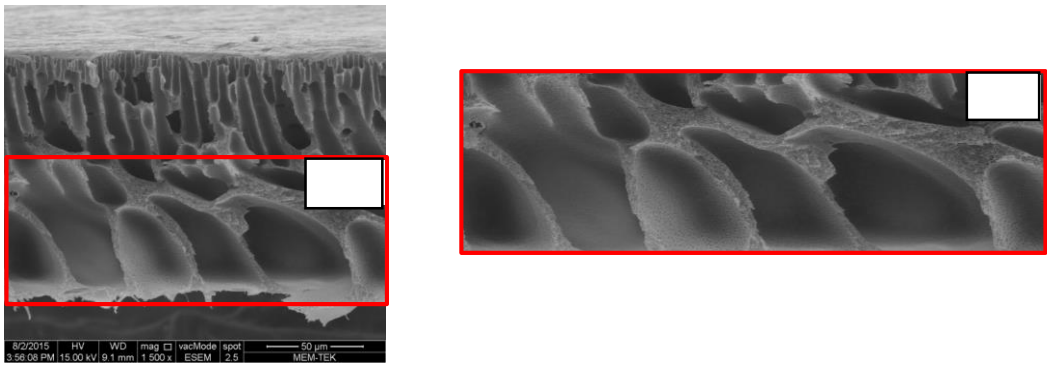
b)



c)



d)



e)

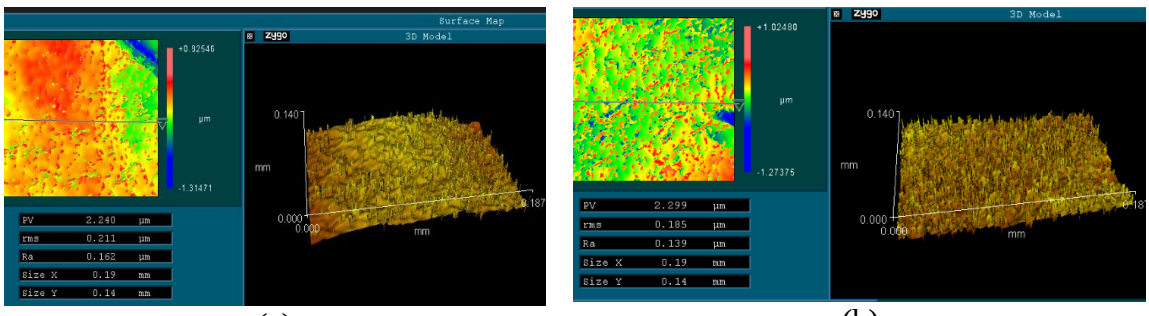
Figure 4.6 : SEM images of (a) Bare PS (b) GO-0.009% (c) GO-0.012% (d) GO-0.024% (e) GO-0.049%.

Concentration of GO affects on membrane morpholgy negatively. It is a clear fact that asymetric morphology of membrane is destroyed by high concentration of GO particules. Higher GO concentration has more molecular weight of particules so accumulation of particules is observed on bottom layer of membrane because of gravitional effect.

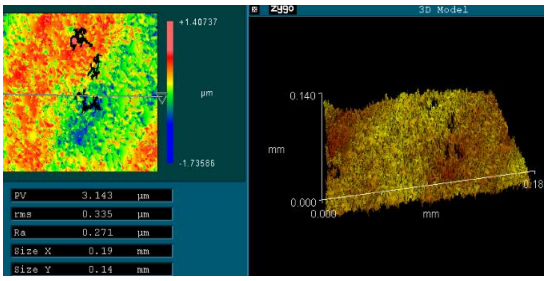
As a result of SEM images, accumulation is high on selective layer in membane of added GO-0.009 % concentration. On the other hand; GO-0.049 % concentration (high nanoparticle concentration) lead to change the direction of pores and damage on pores on bottom layer. In the light of this inferences and also considering permeability results; optimum SEM pictures is chosen GO-0.012 % concentration.

4.6.2 Optic profilometre analysis

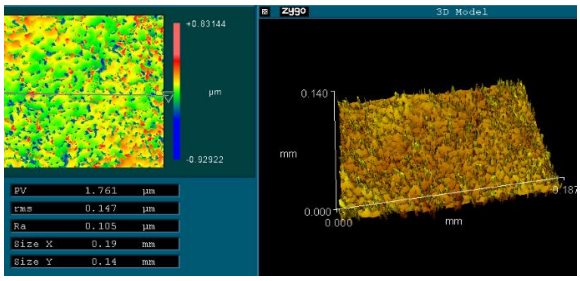
Optic profilometer analyses were done for each produced membrane. Images obtained from the profilometer measurements of membranes are shown according to the GO ratios, in Figure 4.7 (a, b, c, d, e).



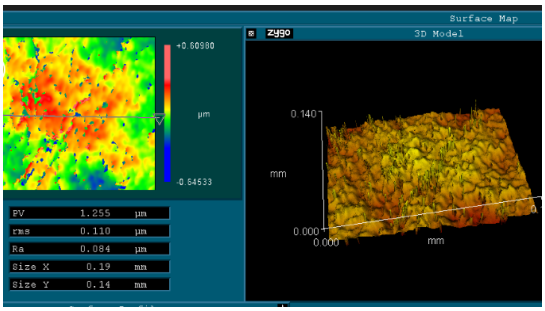
(a) (b)



(c)



(d)



(e)

Figure 4.7 : Surface roughness images of (a) Bare PS (b) GO-0.009% (c) GO-0.012% (d) GO-0.024% (e) GO-0.049%.

The Root Mean Square (RMS) roughness is the root mean square average of the roughness profile ordinates (Rubert, 2016). Route mean square (Rms) values, measured by the optic profilometer analysis, are given for bare membranes in Table 4.4. Lowest roughness value was measured for GO-0.009 %.

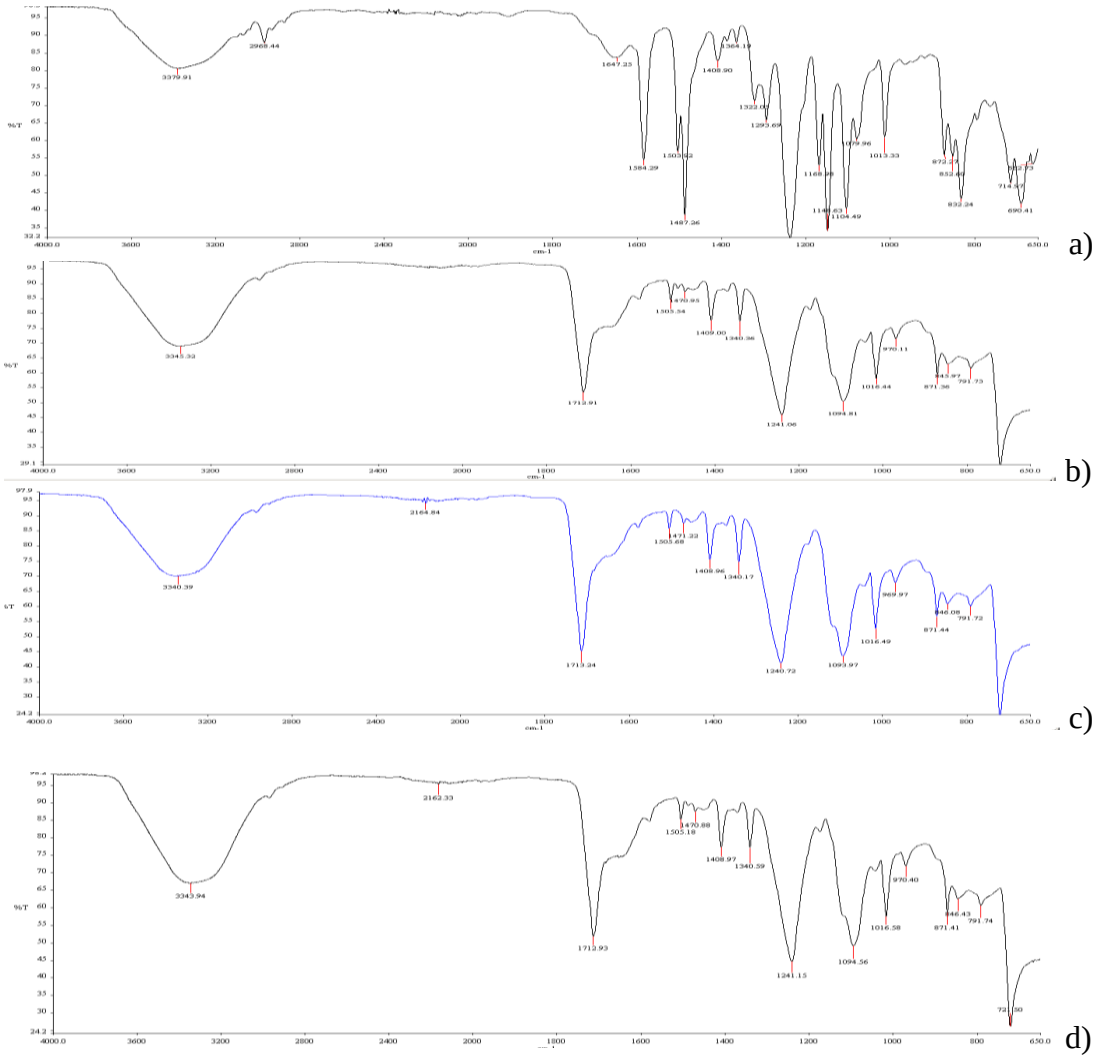
Table 4 .4 : Rms values of the bare membranes.

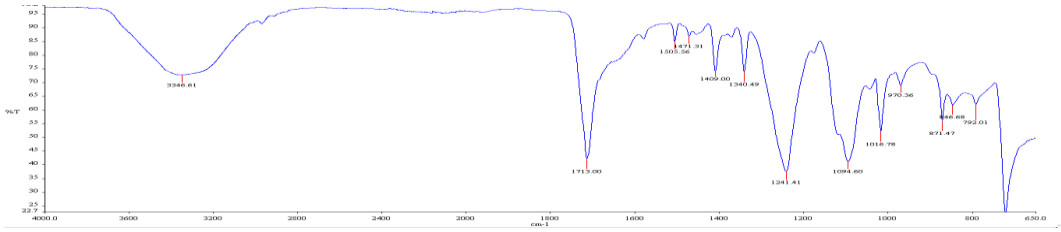
Membrane type	**Rms (µm)**
PS	0.21
G0-0.009%	0.12
G0-0.012%	0.15
G0-0.024%	0.33
G0-0.049%	0.19

The bare membrane will be easier fouled with a higher roughness owing to contaminants accumulating in the rough membrane surface (Zhao et al., 2013). In our GO/PS nanocomposite membranes large valleys were replaced by small ones, and this provides to the smooth of membrane surface. Generally, in higher GO containing membranes the roughness is also higher than the lower GO containing ones.

4.7 Fourier transform infrared spectroscopy (FTIR)

The spectra shown in Figure 4.8, it can be observed that the peak intensities at 3340 and 1712 cm^{-1} increase with the increase in GO concentration. These are characteristic peaks of GO and it is seen that GO is well dispersed. The band at 1712^{-1} cm is attributed to C=O. The broad band between 3000 and 3650 cm^{-1} is attributed to O–H functional group stretching from the graphene oxide surface. The absorption band of PSf at 1293 cm^{-1} corresponds to the O=S=O asymmetric stretching while the peak at 1148 cm^{-1} corresponds to symmetric stretching of O=S=O. The weak peaks between 2850 and 3200 cm^{-1} correspond to aliphatic and aromatic groups. The absorption band at 1241 cm^{-1} is attributed to asymmetric stretching of C–O–C groups.





e)

Figure 4.8: FTIR spectra of (a) Bare PS (b) GO-0.009% (c) GO-0.012% (d) GO-0.024% (e) GO-0.049%

4.8 Antibacterial Performance Results of the Membranes

Sun et al., showed that the antibacterial activity of GO is considered to be a result of membrane stress induced by sharp edges of graphene oxide nanosheets. The formation of hydrogen bonding between oxygenate groups of GO and the lipopolys accharide strings of the cell membrane facilitated to wrap GO nanosheets to bacteria cell membrane, preventing the cells from intaking nutrient, and leading to the cell death. GO can effectively inactivate adhered microorganisms according to contact-killing, while bacterial adhesion on membrane surface is inevitable (Sun et al., 2015). Yu et al., used to GO nanosheets modified with hyperbranched polyethylenimine (HPEI) to enhance the compatibility between GO nanosheets and polymer macromolecules. The number of colonies on the plates treated with HPEI/PES hybrid membranes did not show a clear change compared with that treated with control membranes. However, the number of colonies on the plates treated with HPEI-GO/PES membranes decreased significantly with a high bacteriostasis rate against E. coli of 74.88% (Yu et al., 2013). When nanoparticle containing membranes were compared, growth circles around the membrane surfaces were smaller than bare membrane. The bacteria numbers around membrane as shown in Figure 4.9. and in Figure 4.10. The reason of this, graphene-based nanomaterials could inhibit the growth of E. coli. The damages can be induced on bacterial cells after direct contact with graphene-based materials because of membrane stress induced on bacterial cells resulting in destruction of cell structures (Yu et al., 2013).

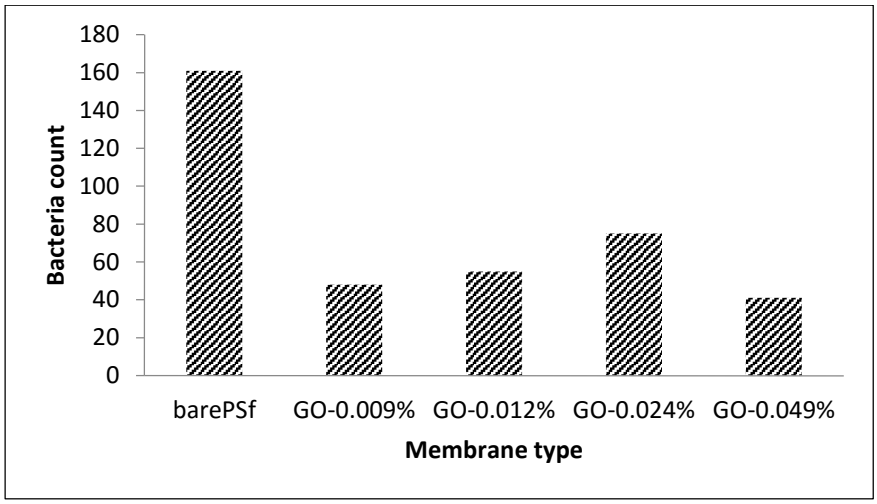
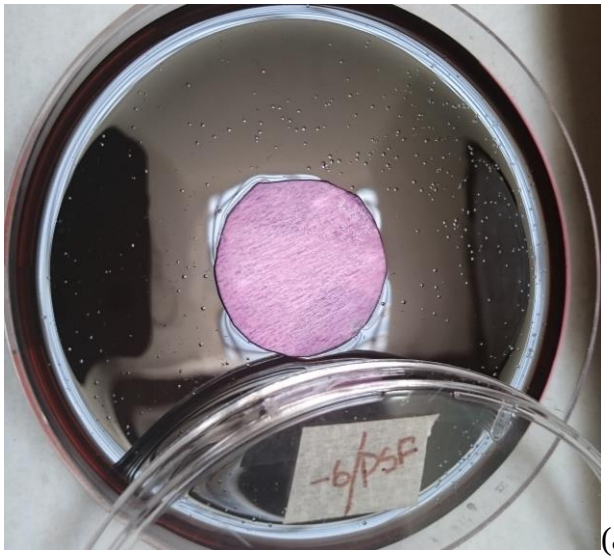
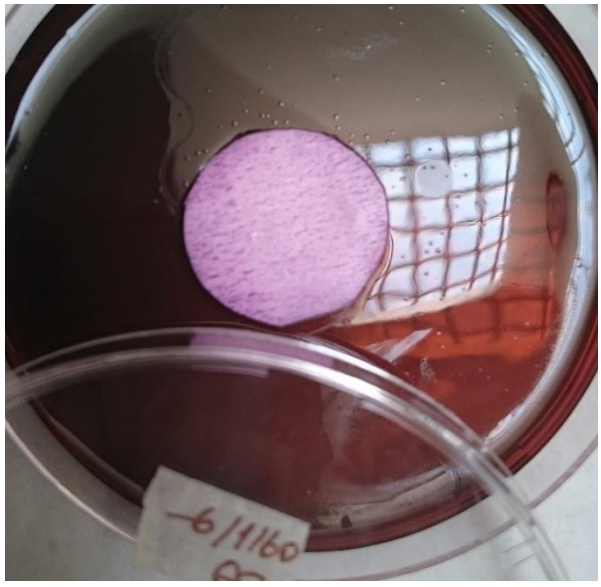


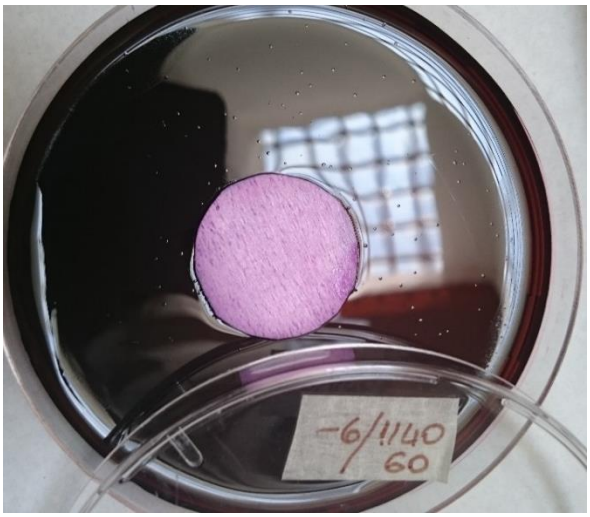
Figure 4.9 : The graph of inhibation ratio



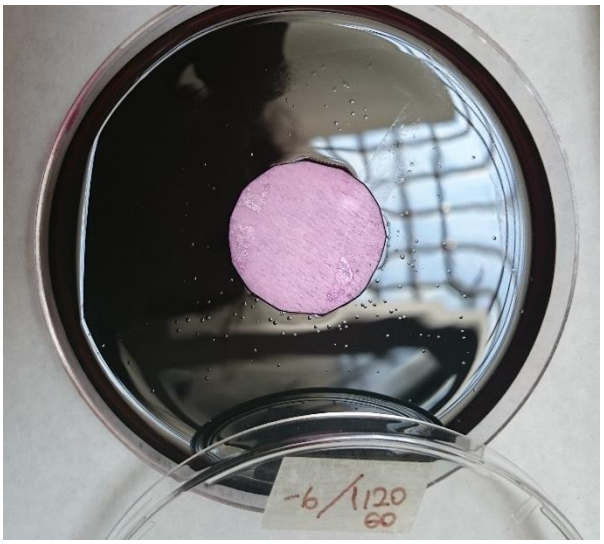
(a)



(b)



(c)



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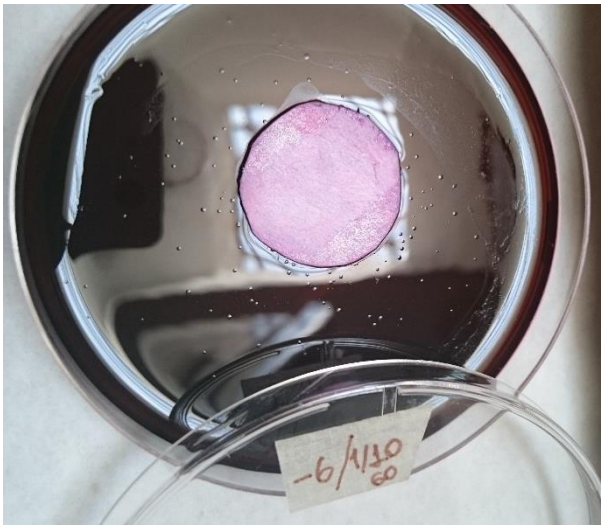

(e)

Figure 4.10 : The images of viability test of (a) Bare PS (b) GO-0.009% (c) GO-0.012% (d) GO-0.024% (e) GO-0.049%

5.CONCLUSION

Results of the performance and characterization tests for the bare and the composite membranes containing GO nanoparticles are given in the Table 5.1.

Table 5 .1 : All characterization results of bare and GO membranes.

Membrane type	Roughness (µm)	Contact Angle (°)	Average Pore size (µm)	Young's modulus (x10^7 Pa)	Surface charge (mV)	Permeability (L/m^2.h.bar)
Bare PSf	0.21	72±5°	0.031	3.46	-19	118±0.07
G0-0.009%	0.12	42±9°	0.029	3.60	-10	123±1.13
G0-0.012%	0.15	44±8°	0.031	4.26	-9	158±18.6
G0-0.024%	0.33	64±6°	0.035	1.88	-26	98±13.8
G0-0.049%	0.19	71±5°	0.034	1.67	-27	142±0.8

From the all results, major findings are listed as follows:

1. Nanocomposite membrane production experiments;

-Addition of GO was increased permeability of PS/GO membranes up to a critical GO concentration and then permeability decreased because of the destruction in the pore structure in higher concentrated GO membranes.

-Produced GO membranes pore size are in the range of UF membranes. Values of membrane porosity experiments did not change much for various NPs but GO-0.049% is the highest pore size. Generally,pore size tend to increase.

-Addition of GO decreased the contact angle value for most of the composite membranes compared to bare membrane. However, in the higher concentration, GO was remained in bottom of the membrane and cause the surface hydrophiliciy is almost same with PS and in the lower concentration surface is more hydrophilic than highest concentrated GO composite membranes.

- Surface charges of membranes measured that the lowest surface charge values were obtained for the GO-0.012%, highest surface charge values were obtained for the GO-0.049%. Generally high GO concentration membranes should have high surface charge because GO is negatively charged. When there is a stacking the overall surface charge of the membrane is clouded and that is why were observed low surface charge. In the other case where there is no stacking of GO on top of each other then were

observed high surface charge with high GO concentrations. GO stacking on top of each other which determines the surface charge and roughness of the membrane.

-In mechanical strength analysis, increasing the amount of GO to GO-0.049% led to weaker mechanical strength due to aggregation of GO in the PS matrix. As a result, mechanical strenght of membrane GO-0.012% concentration is higher than other membranes.

-Roughness was decreased by the addition of NP for GO membranes. Generally, in higher GO containing membranes the roughness is also higher than the lower GO containing ones.

-As a result of SEM images, accumulation is high on selective layer in 0.009 % GO membrane. On the other hand; 0.049 % GO membrane lead to change the direction of pores and damage on pores on bottom layer. 0.012 % GO membrane has better SEM pictures. The pore structure is finger-like in all membranes.

-FTIR results showed that the peak intensities at 3340 and 1712 cm^{-1} increase with the increase in GO concentration. These are characteristic peaks of GO and it is seen that GO is well dispersed.

2. Membrane antibacterial experiment;

-At the end of viability experiments, nanocomposite membranes were compared and resulted that membranes produced with GO had a smaller growing ring around the membrane.

Consequently, 0.012 % GO nanocomposite membrane have the optimum properties according to characterization and antibacterial test results.

GO has been used in different ways to improve membrane properties for water and wastewater treatment. It can be observed that GO composite membranes have much better properties including increased mechanical strength, antimicrobial property, permeability, hydrophilicity etc. In this study, GO showed its improved characterization results and antibacterial performances. However, more work must be done to understand the antibacterial and anti-biofouling mechanism. Especially, anti-biofouling property must be tested by using these GO composite membranes in the membrane bio reactor system.

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